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# Conducting Polymers From Heterocyclic Compounds

A thesis presented for the degree of Doctor of Philosophy of The  
Open University

by

Gang Hu

The Open University  
Chemistry Department  
October, 1994

Date of submission: 16<sup>th</sup> November 1994  
Date of award: 20<sup>th</sup> February 1995

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**To My Wife And Our Daughter**

## Declaration

The work described herien was carried out at The Open University in Milton Keynes between September 1990 and August 1994.

It has been done independently and submitted for no other degree.

-----  
Gang Hu

October 1994

## Acknowledgements

I would like to express my gratitude to Dr P. G. Taylor for his encouragement and advice throughout the course of this study.

I acknowledge with thanks my colleagues in The Chemistry Department and Cookson Technology Centre for their invaluable discussions and to the departmental technical staff for practical help given.

I am also grateful to Cookson Company and The Open University for the financial support to carry out this work.

I am truly thankful to my wife for her encouragement.

## Abstract

The novel electroactive polymers poly(5,6-dimethylisothianaphthene) (PDMITN) and poly(4-methoxyisothianaphthene) (PMeOITN) have been synthesised. As with polyisothianaphthene (PITN), PDMITN can be obtained by both electrochemical and pure chemical oxidation from the monomers 5,6-dimethylisothianaphthene (DMITN) and 5,6-dimethyl-1,3-dihydroisothianaphthene (DMDHITN). Using a nucleophilic electrolyte, tetrabutylammonium bromide (TBNBr), and dichloromethane the conductivity of PDMITN was as high as  $100 \text{ Scm}^{-1}$ . The polymer film undergoes a high contrast colour change from blue in the neutral form to yellow/transparent in the oxidised form. PMeOITN, however, can only be prepared by electrochemical oxidation from the monomers 4-methoxyisothianaphthene and 4-methoxy-1,3-dihydroisothianaphthene when a non-nucleophilic electrolyte, tetraethyl ammonium tetrafluoroborate (TENBF), is used. PMeOITN is soluble in dichloromethane and chloroform, but, the polymer film does not undergo a strong colour change unlike PDMITN and PITN.

The properties of PDMITN and PMeOITN have been investigated using FT-IR, NMR, UV/Vis-near IR, X-ray powder diffraction and Cyclic voltammetry and compared with those of PITN.

The consumption of monomers and the formation of intermediates during electrochemical and chemical oxidation of the isothianaphthene derivatives were examined using cyclic voltammetry, time-resolved electronic absorption spectrometry and HPLC. The presence of methyl and methoxy groups does indeed affect the polymerisation process.

Silicon containing monomers including 1,1,3,4-tetramethyl-1-sila-3-cyclopentene (TMSCP), 1,1,3,4-tetramethylsilacyclopentadiene (TMSCPD) and 1,1-dimethyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene (TPSCP) have been successfully synthesised in good yield. Attempts to polymerise these silicon containing compounds have been carried out.

## Abbreviations

|              |   |
|--------------|---|
| CB           | conduction band                                   |
| d            | doublet   |
| DHITN        | 1,3-dihydroisothianaphthene                       |
| DMDHITN      | 5,6-dimethyl-1,3-dihydroisothianaphthene          |
| DMITN        | 5,6-dimethylisothianaphthene                      |
| $\delta$     | chemical shift (in ppm)                           |
| E            | potential   |
| ECE          | charge transfer-chemical reaction-charge transfer |
| $E_{1/2}$    | half-wave potential in voltammetry                |
| EI           | electron impact                                   |
| $E_p^a$      | anodic peak potential                             |
| $E_p^c$      | cathodic peak potential                           |
| Et           | ethyl   |
| FT-IR        | Fourier transform infrared spectroscopy           |
| GC           | gas chromatography                                |
| GPC          | gel permeation chromatography                     |
| HCB          | hexachlorobutadiene                               |
| HPLC         | high performance liquid chromatography            |
| $i_p^a$      | anodic peak current                               |
| $i_p^c$      | cathodic peak current                             |
| ITN          | isothianaphthene                                  |
| ITO          | indium-tin oxide coated glass                     |
| J            | coupling constant (in Hz)                         |
| v            | scan rate (mv/cm)                                 |
| $\nu_{\max}$ | wavenumber ( $\text{cm}^{-1}$ )                   |
| m            | multiplet   |



|           |   |
|-----------|---|
| Me        | methyl  |
| MeCN      | acetonitrile  |
| MeODHTN   | 4-methoxy-1,3-dihydroisothianaphthene                             |
| MeOITN    | 4-methoxyisothianaphthene   |
| mv        | millivolts  |
| NMR       | Nuclear Magnetic Resonance  |
| PDMITN    | poly(5,6-dimethylisothianaphthene)                                |
| PhITN     | phenanthrenethiophene   |
| PhITNCOOH | phenanthrenethiophene dicarboxylic acid                           |
| PITN      | poly(isothianaphthene)  |
| PMeOITN   | poly(4-methoxyisothianaphthene)                                   |
| Pt        | Platinum  |
| q         | quartet   |
| R         | alkyl or aryl group   |
| $\sigma$  | conductivity ( $\text{ohm}^{-1}\text{cm}^{-1}$ or $\text{s/cm}$ ) |
| S         | $\text{ohm}^{-1}$   |
| t         | triplet   |
| TENTS     | tetraethylammonium p-toluenesulphonate                            |
| TENBF     | tetraethylammonium tetrafluoroborate                              |
| TBNBP     | tetrabutylammonium hexafluorophosphate                            |
| TBNBr     | tetrabutylammonium bromide  |
| TBNHS     | tetrabutylammonium hydrogen sulphate                              |
| TBNI      | tetrabutylammonium iodide   |
| TCB       | 1,1,4,4-tetrachlorobutadiene                                      |
| THF       | tetrahydrofuran   |
| TMSCP     | 1,1,3,4-tetramethyl-1-sila-3-cyclopentene                         |
| TMSCPD    | 1,1,3,4-tetramethylsilacyclopentadiene                            |
| TPSCP     | 1,1-dimethyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene            |

**VB**

**valence band**

**UV/Vis.**

**ultraviolet and visible**

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# Chapter One

## Introduction

### 1.1 The Theoretical Aspects of Conducting polymers

#### 1.1.1 Conduction in solid materials

Generally, electrical conduction occurs by the long range migration of either electrons or ions. For any material and charge carrier the conductivity is given by:

$$\sigma = N | e | \mu$$

where  $\sigma$  represents the conductivity ( $\text{ohm}^{-1} \text{cm}^{-1}$  or  $\text{Scm}^{-1}$ ),  $N$  is the number of charge carriers per unit volume;  $|e|$  is the charge on the carriers and  $\mu$  is the mobility of the charge carriers<sup>1</sup>.

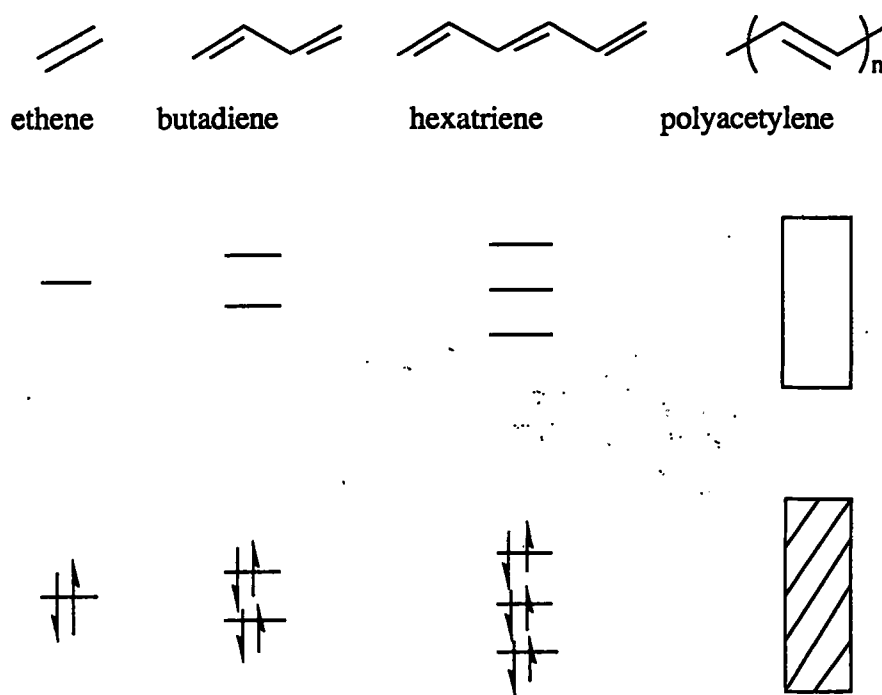
The high conductivity of metals arises from the high density of charge carriers and the extremely high mobility of the charge carriers. In most organic materials low conductivity arises from the low mobility of the charge carriers, even though there may be a high density of charge carriers in the system.

#### 1.1.2 Conduction mechanisms in conjugated polymers<sup>2-10</sup>

In conventional polymers, just as in crystals, the low mobility of charge carriers results from the interaction of a polymer unit cell with all its neighbours leading to the formation of electronic bands which limit the freedom of travel of the charge carriers. The highest occupied electronic levels are associated with the valence band (VB) and the lowest unoccupied electronic levels are related to the conduction band (CB). The electronic band width between VB and CB is referred to as the energy gap. This

contributes to the intrinsic electrical conducting properties of the polymer. Thus, conventional polymers are insulators due to their large energy gaps.

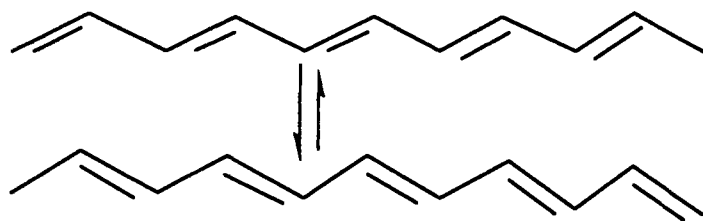
Interestingly, polymers with an extensive conjugated backbone will have a high potential conductivity due to a highly delocalised molecular orbital system. As the conjugation length increases the energy gap will be reduced. Polymers can become highly conducting by creation of a subgap between the VB and CB via a p or n doping process (oxidation or reduction). Scheme 1-1 shows that as we progress from ethene, butadiene, hexatriene to polyacetylene the band gap gradually decreases with the accompanying increase of conjugation. Since it is so simple, polyacetylene is often used as an example to describe in the conduction mechanism of conjugated polymers<sup>2,3</sup>.



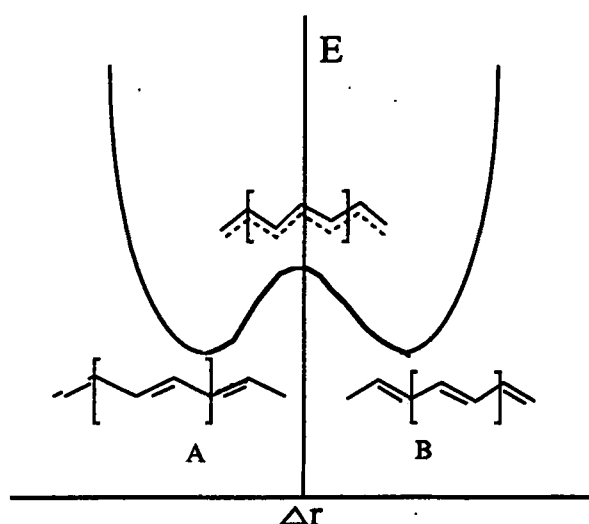
Scheme 1-1 Change of band gap in organic molecules

Polyacetylene exists in two configurational states (*trans* and *cis*). All *cis*-polyacetylene is less thermodynamically stable than all *trans* and can be isomerised to the *trans* form even at room temperature. All *trans*-

polyacetylene has a degenerate ground state, that is there are two forms that have the same energy, but which differ from each other as a result of alternation of the carbon-carbon single and double bonds, as shown in Scheme 1-2 a and b.



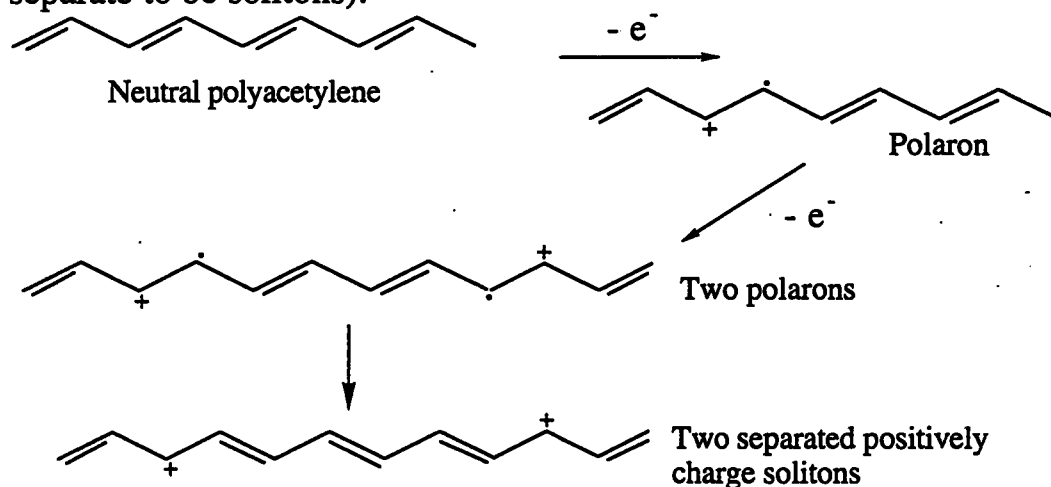
Scheme 1-2a Two forms of neutral all *trans*-polyacetylene



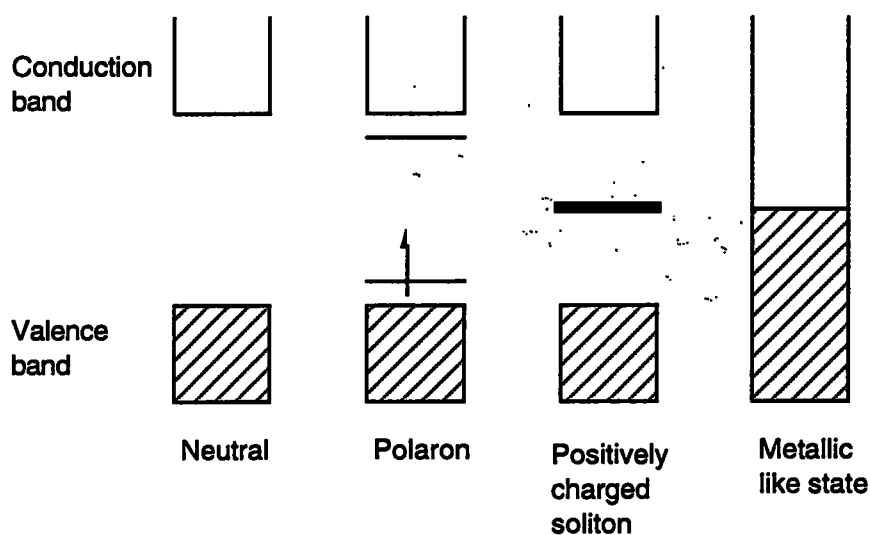
Scheme 1-2b Total energy curve of all *trans*-polyacetylene as a function of degree of bond length alternation( $\Delta r$ ).

Magnetic resonance studies of neutral all *trans*-polyacetylene show that there are some highly mobile neutral magnetic defects in the chain. These arise from bond-alternation domain walls induced upon isomerisation. This defect, which resembles a free radical, is called a neutral soliton. When the polymer is oxidised an electron is removed from the polymer system to form a radical cation (spin 1/2) which is associated with a lattice distortion and results in the presence of a localised electronic state in the band gap. The cation-radical and the resulting structural reorganisation should not be considered independently as they are inseparable. Considered together as a

single entity they are called a polaron. As the extent of oxidation increases the number of radical cations increases. As the concentration of radical cations in the system increases the polaron state becomes less stable with respect to spin recombination. Thus, further oxidation leads to the formation of a new charged species, a pair of charged solitons (as a result of the degeneracy, the two charges formed in *trans*-polyacetylene can readily separate to be solitons).



Scheme 1-3a Formation of polarons and solitons



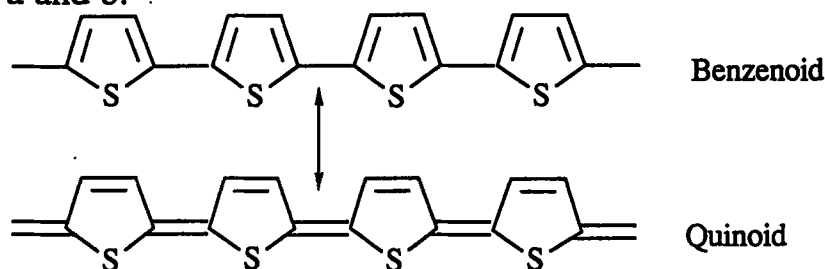
Scheme 1-3b Band structures of neutral and oxidised polyacetylene

This is illustrated in Scheme 1-3 a and b. The formation of charged solitons results in the appearance of localised electron levels at the centre of the band gap. Ultimately, it is possible that the charged solitons may overlap leading

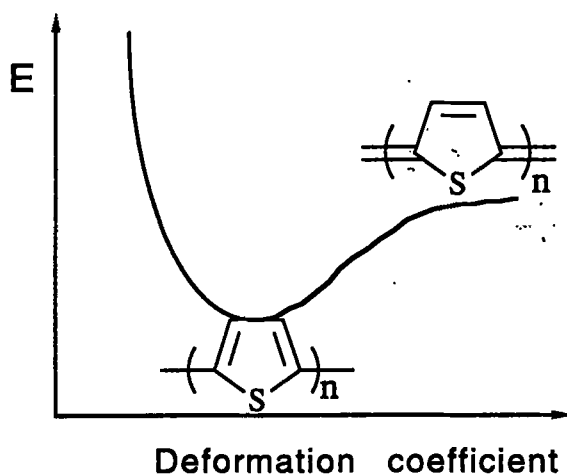


to the closure of the band gap. Thus, a metallic like material is produced if a very high level of doping is achieved. This creates an effective bridge between the VB and CB to allow the charge carriers to pass freely to some extent. Thus doped polyacetylene has a very high conductivity.

Unlike all *trans*-polyacetylene, polyheterocycles such as polythiophene and polypyrrole, have non-degenerate ground states. Taking polythiophene as the example, whilst it can exist in two canonical forms, benzenoid and quinoid, the fully aromatic benzenoid state is more stable than the quinoid state. Thus, they do not have the same energy level, as shown in Scheme 1-4 a and b.



Scheme 1-4a Aromatic and quinoid forms of polythiophene.

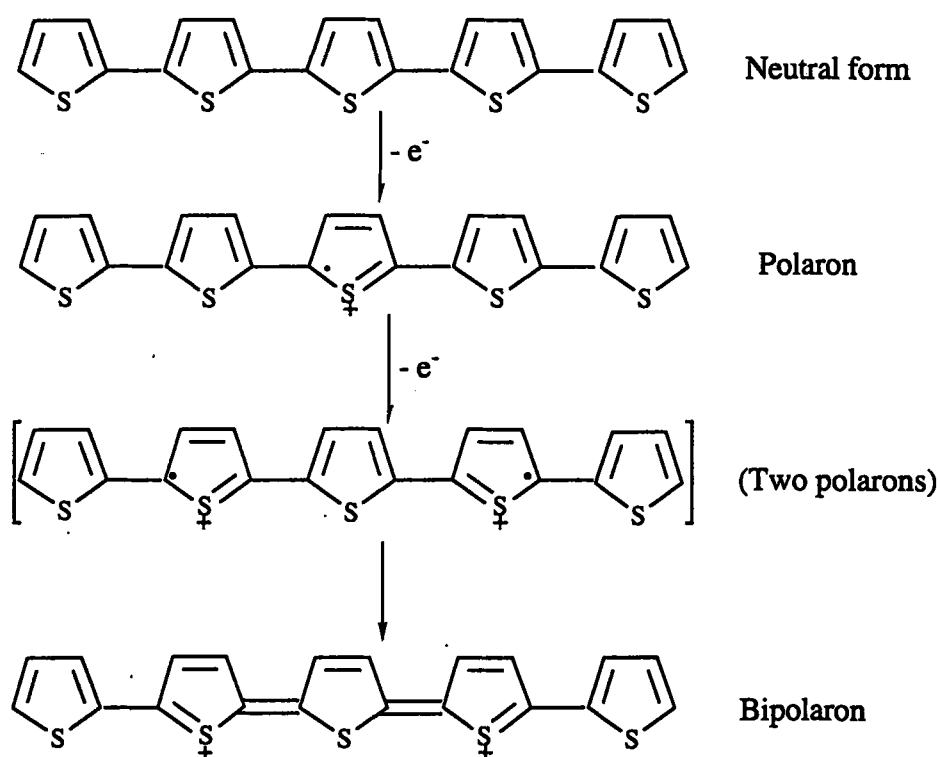


Scheme 1-4b Total energy diagram for the aromatic and quinoid forms of polythiophene.

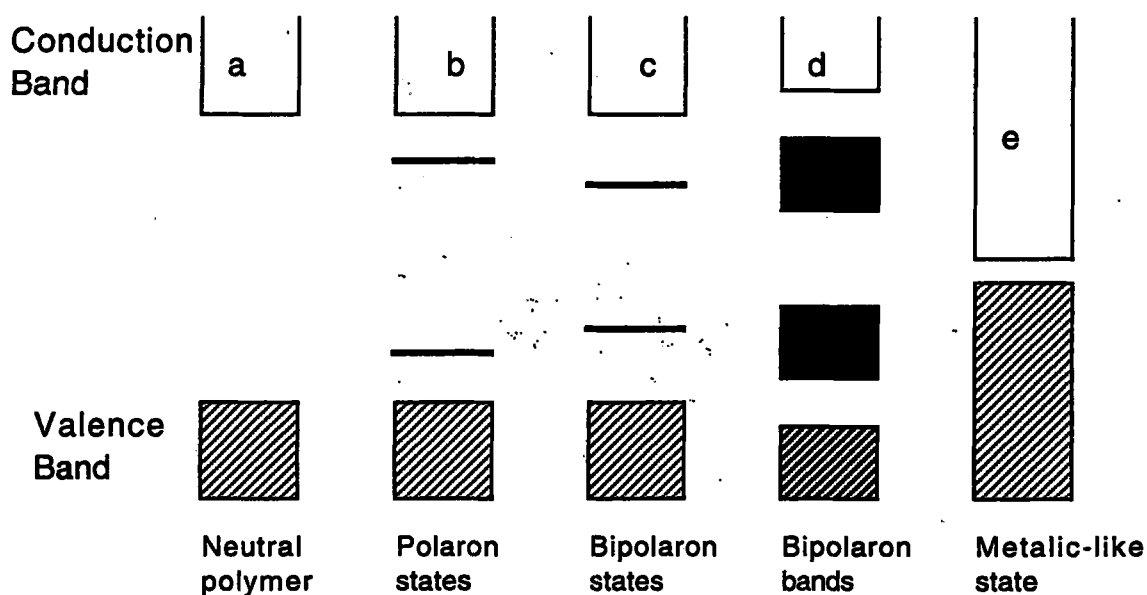
As a consequence, a slightly different doping mechanism has been proposed, which is again related to the formation of polarons and bipolarons. On oxidation an electron is taken from the polymer chain to form a radical cation, a polaron. This species has been confirmed by ESR studies. At this

relatively low oxidation level the coulombic repulsion of these positively charged polarons prevents the combination of the free radicals on the chain. However, if further doping is carried out, the ESR signal from the polaron rapidly decays even though the system is highly conductive. It has been suggested that when a second electron is removed from the chain to yield two polarons, this is not stable and collapses to give a dication known as a bipolaron (spinless), since the lattice relaxation around the two charges is much stronger than around only one charge. This is depicted in Scheme 1-5 a and b.

Formation of the polaron and bipolaron each leads to two localised electronic states in the band gap. The lower polaron state is half filled and the upper one is empty, whereas both of the bipolaron levels are unoccupied. Thus, the presence of polarons in the polymer chain is expected to give three optical transitions below the  $\pi-\pi^*$  interband transition threshold. However, the presence of bipolarons leads to two subgap transitions. As more electrons are taken out, the bipolaron states overlap and broaden into bands. However, they cannot create mid-gap states in the centre of the band gap. In other words, the band gap of polythiophene cannot be closed to give a metallic state. Thus, the conductivity of polythiophene will be lower than that of polyacetylene. Although the conductivity of polythiophene will be lower than that of polyacetylene, it has a unique advantage in that it is more stable to air and moisture than polyacetylene. Hence, until now, polythiophene and its derivatives have been the most popular type of conducting material to be investigated.



Scheme 1-5a Formation of polaron and bipolaron in polythiophene chain.



Scheme 1-5b Energy band diagrams for polythiophene with nondegenerate state<sup>10</sup>.

The above description of the conduction mechanisms in polyacetylene and polythiophene is a summary of one of several models based on the concept of soliton, polaron and bipolaron. A number of criticisms<sup>11,12,13</sup> have been made about this model. One is that there is no real energy gain in the

transformation from the polaron to the bipolaron state. Thus, the formation of either state is energetically equivalent. A second criticism is that any deviation from the regular carbon backbone structure would prevent the formation of bipolarons.

It is important to note that the above explanation only accounts for conduction along the polymer chain, that is one dimensional electronic transport. If the polymer has a high conductivity the electron transport between the polymer chains, interchain transport, must also be capable of efficient movement of charge carriers. It is possible that interchain conduction is the rate limiting step in all conducting polymer systems. This also predicts that bipolarons should be able to hop between chains<sup>4,9</sup>.

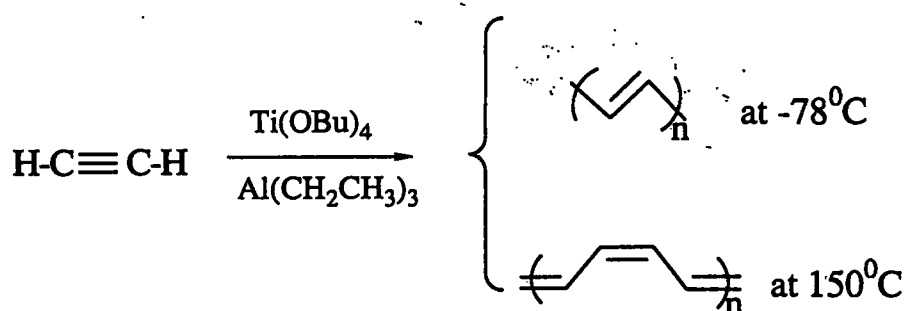
## **1.2 Synthesis of Conducting Polymers**

Since the discovery that conjugated macromolecules could be converted into electrical conducting materials by n or p doping (oxidation or reduction), the subject has attracted a significant amount of attention from scientists in many areas. Organic chemists, electrochemists, material scientists and solid state physicists have searched for better novel conjugated compounds, examined the relationship between the structure and properties and explored new applications. As a result a large number of conjugated compounds and their polymers have been made, including polyacetylene ( the simplest among all conjugated polymers with linear alternating single and double carbon-carbon bonds), aromatic C-C ring backbone polymers ( polyazulene, polyphenylene and its derivatives), polyheterocycles (polypyrrole, polythiophene, polyfuran and their derivatives). The combination of more than one of the above compounds has created a range of new copolymers.

### 1.2.1 Polyacetylene

It was the discovery of highly conducting polyacetylene that launched this fascinating area of research almost twenty years ago. Polyacetylene is a very simple macromolecule which exhibits a range of electrical properties. Even now, it is still studied to examine the basic electrical conducting mechanism of conjugated polymers.

In the later 50's Natta<sup>14</sup> first made polyacetylene as a black powder. It was insulating and insoluble. No detailed characterisation of this black powder was reported. Fortunately in 1974 a silvery looking film with a highly crystalline form was accidentally prepared by Hideki Shirakawa in Japan<sup>15</sup> using a Ziegler-Natta polymerisation catalyst. The reaction scheme is shown in Scheme 1-6. This provided a route to a material that could be characterised more readily. FTIR was able to show that the structure could be all *cis* or *trans* depending on the reaction temperature. This successful work provided a catalyst to further studies to examine its full potential, although, at this time, the polymer film was still considered to be an insulator.



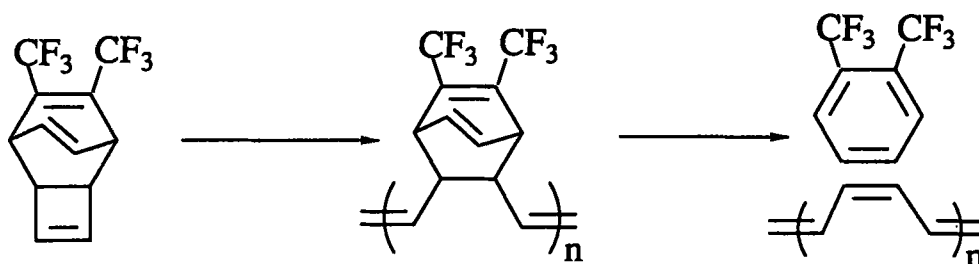
Scheme 1-6 Polymerisation of acetylene to give *cis* and *trans* isomers.

A major breakthrough took place in 1977 when Shirakawa, MacDiarmid and Heeger discovered that the insulating polyacetylene film became highly conducting<sup>16,17,18</sup> when exposed to strong oxidants such as iodine.

Shirakawa's method continues to be the most common way of synthesising

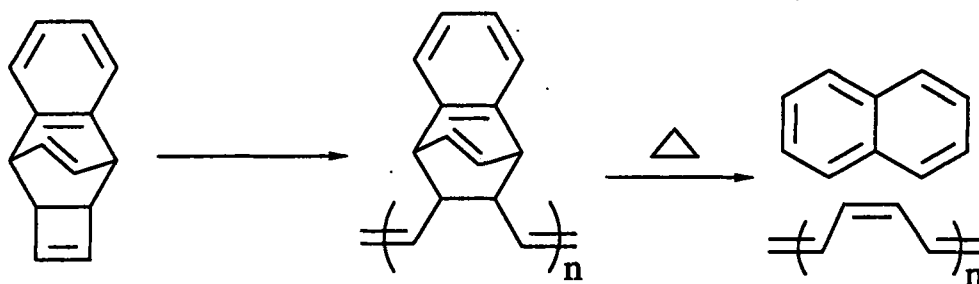
polyacetylene and the polymer made from this procedure is often called S-PA (Shirakawa polyacetylene). Based on Shirakawa's method Naarman and coworkers<sup>19</sup> polymerised acetylene in silicon oil using the same Ziegler-Natta catalyst. When the film was stretched up to 400% and doped, a homogeneous, defect-free polyacetylene film was formed with a very high conductivity of more than  $10^5 \text{ Scm}^{-1}$ .

However, although the polymer produced by this method had a high conductivity, there were crucial disadvantages: firstly it was very sensitive to air and moisture and secondly it was difficult to process. To solve these problems Feast<sup>20,21,22</sup> prepared the same polymer via a different route. The process is called retro-cycloaddition and involves a ring-opening metathesis polymerisation using a range of active catalysts such as  $\text{WCl}_6$ ,  $\text{MoCl}_5$  or metallocarbene species. The prepolymer made by this method is soluble in common organic solvents and can also be purified by conventional reprecipitation techniques. The first successful preparation was the metathesis polymerisation of 7,8-bis(trifluoromethyltricyclo [4,2,2]deca-3,7,9-triene, illustrated in Scheme 1-7. Exothermic decomposition converts the prepolymer into a high quality polyacetylene with relatively low crystallinity. The low crystallinity is especially useful in nonlinear optical applications where the scattering of light by crystals becomes a problem. To improve its conductivity the crystallinity can be increased by orienting the prepolymer film, cast from the solution system, before converting it to the polyacetylene<sup>23,24</sup>.



Scheme 1-7 A retro-cycloaddition route to polyacetylene

This prepolymer has one problem in that the decomposition of the benzenoid unit occurs fairly readily. The elimination takes place even below room temperature, so that the preparation needs to be carried out at low temperatures. To increase the stability of the prepolymer an alternative system was used as shown in Scheme 1-8. It was reported that the resulting prepolymer is unquestionably stable at room temperature. The elimination of naphthalene takes place at over 700°C to form polyacetylene as expected.

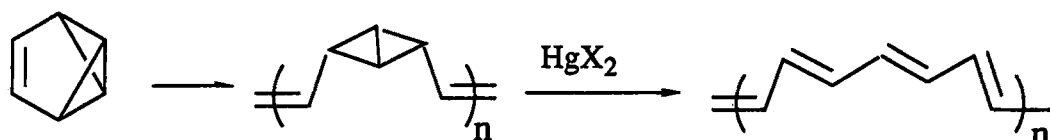


Scheme 1-8 An alternative retro-cycloaddition route to polyacetylene

Although the process provides a novel route to the conjugated polymer, readily allowing fabrication and processing to give the final products, the mass loss is very high ( a benzenoid unit or naphthalene ) during the conversion. This could decrease the quality of the final polyacetylene products.

To minimise the mass loss during the conversion, Swage and Grubbs<sup>25</sup> used benzvalene as the starting material. The metathesis polymerisation of benzvalene gives a prepolymer with considerable ring strain. By using a

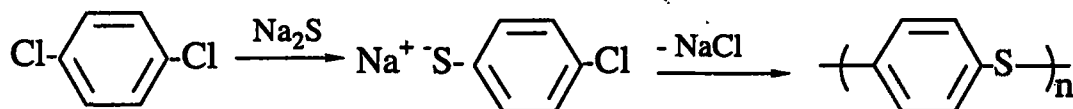
mercury salt the prepolymer can be converted to polyacetylene as shown in Scheme 1-9. The process has the advantage that no mass loss occurs upon conversion. However, the polyacetylene product doped with iodine has a relatively low conductivity. The  $C^{13}$  CP-MAS NMR data indicate that there were a number of saturated ( $sp^3$ ) defects in the product, possibly due to cross-linking created by residual mercury salts.



Scheme 1-9 Polybenzvalene and its polymer

### 1.2.2 Phenylene backbone Polymers

A number of conjugated polymers are known based on an aromatic C-C backbone. Examples are polyparaphenylene(PPP), polyphenylene sulphide(PPS) and their derivatives. They can be synthesised by a chemical step-growth polymerisation or electrolysis. Polyphenylene sulphide is a commercial product sold as a thermoplastic<sup>28</sup> under the trade name of 'Ryton' by the Phillips Petroleum Company. Polyphenylene sulphide is typically prepared by condensation of dichlorobenzene with sodium sulphide in N-methylpyrrolidone as shown in Scheme 1-10.



Scheme 1-10 Condensation to polyphenylene sulfide

The resulting polymer was found to be soluble in high boiling solvents and environmentally stable, thus is easily processable. Baughman and coworkers re-examined this polymer and reported that doping the polymer with  $SO_3$  increases the conductivity to up to  $80 \text{ Scm}^{-1}$  even though the degree of polymerisation is moderate ( $M_n \approx 11000$ )<sup>26,27</sup>. Another example is

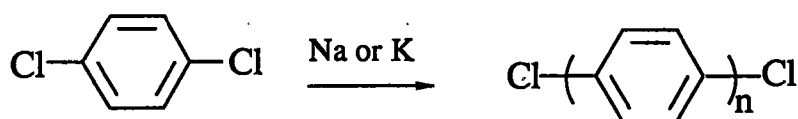


polyparaphenylene which can be prepared by a range of condensation polymerisation routes. The coupling reaction can be carried out using reactions such as the Wurtz-Fittig<sup>29</sup>, Ullmann<sup>30</sup>, Grignard<sup>31</sup>, Diazonium<sup>32</sup> and direct oxidative coupling<sup>20</sup>. The reactions are outlined in Scheme 1-11.

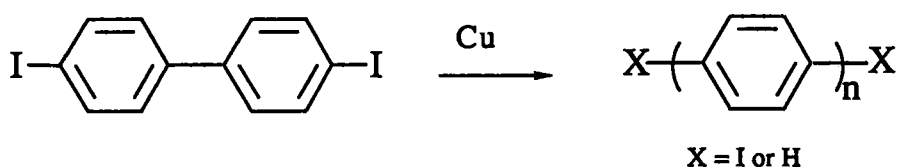
The polymer made through reactions a and b is soluble but has a low molecular weight. The polymer produced via a Grignard coupling is thermally stable with a high decomposition temperature of over 500°C, however, it is only partially soluble. Direct oxidative coupling using various Lewis-acid reagents to perform an oxidative cationic condensation seems to be the most effective and simple. IR studies of PPP and its pyrolysis products shows that 1,4-coupling is the predominant reaction.

The main problem with such polymerisations is the presence of chain-growth terminating side reactions such that the resulting polymers tend to have a very low molecular weight and they can be insoluble.

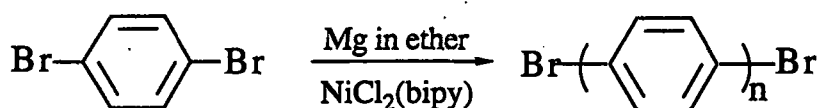
(a) Wurtz-Fittig coupling



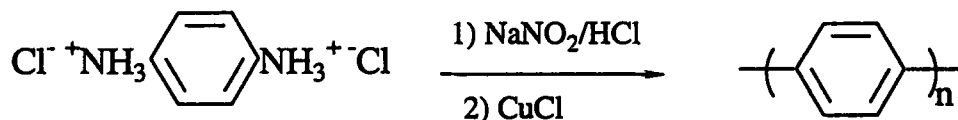
(b) Ullmann coupling



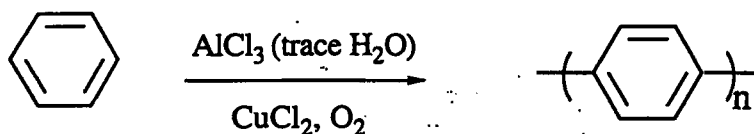
(c) Grignard coupling



(d) Diazonium coupling

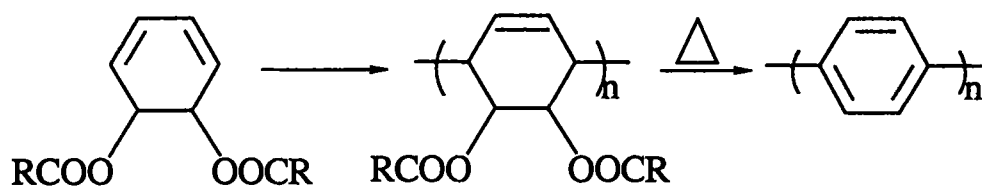


(e) Oxidative coupling



Scheme 1-11 Polyparaphenylene synthesis

Drawing on the experience of making polyacetylene from a prepolymer, a new route has been developed<sup>34,35</sup> using a *cis*-dihydrocatechol derivative of cyclohexadiene, that is easily obtained from a microbial oxidation of benzene. This can be converted to a soluble prepolymer by radical initiated polymerisation. The prepolymer can be converted thermally at 250-300°C (if R is a methyl group) to polyparaphenylene with loss of alcohol or acetic acid. The reaction is outlined in Scheme 1-12.



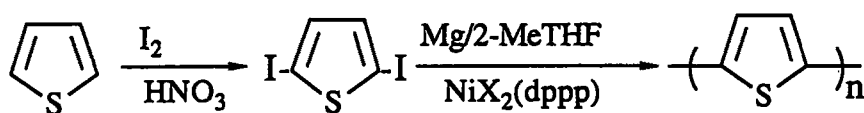
Scheme 1-12 A precursor route to polyparaphenylene

Not only can polyparaphenylene be produced by pure chemical coupling but it can also be made by an electrochemical coupling. Electroreduction of 4,4'-dibromobiphenyl in the presence of a nickel catalysts<sup>36</sup> leads to homogeneous PPP films being deposited on the electrode. It was also reported that benzene could be directly polymerised by electrooxidation using hydrofluoric acid as an electrolyte in sulphur dioxide. The resulting polymer has an irregular structure similar to the polymer produced by the Lewis acid, aluminium chloride, oxidation<sup>37</sup>.

### 1.2.3 Polyheterocycles

Although there are many well developed synthetic routes which give highly regular polyacetylene and polyphenylene with a high conductivity after doping, one fatal weakness of these polymers is their susceptibility to air and moisture. It is therefore desirable to develop other types of conjugated polymers which are stable to air and moisture, and which can be reversibly oxidised under a range of conditions. Conjugated heterocyclic compounds were therefore investigated, including pyrrole, furan, thiophene and their derivatives. Owing to the stability of the doped and neutral states, polymers of thiophene have been extensively examined, in particular, the synthesis of the polymers, their electrochemical activity and their solid state physical characteristics. Polythiophene can be prepared by both chemical coupling and electrochemical polymerisation. The chemical coupling includes Grignard coupling with a nickel catalyst<sup>38,39</sup> (outlined in Scheme 1-13), organocuprate coupling<sup>40</sup>, Friedel-Crafts alkylation<sup>41</sup> and direct oxidation

with ferric chloride<sup>42</sup>. The Grignard coupling is often favoured since it forms a thiophene polymer with a regular  $\alpha, \alpha'$  linkage. First, 2,5-dihalo thiophene was reacted with one equivalent of magnesium in Me-THF to form a dicarbanion. This was followed by the introduction of a coupling catalyst, such as a nickel(II) complex, to accelerate the coupling reaction to give the long chain polythiophene with regular  $\alpha, \alpha'$  linkages. Direct oxidation with  $\text{FeCl}_3$  leads to the formation of some  $\alpha, \beta$  linkages and hence an irregular structure. The final products from all these coupling processes always contained some trace catalyst residues which were difficult to remove. This is particularly true for the synthesis of the insoluble parent polythiophene.



Scheme 1-13 Nickel-catalysed Grignard coupling of thiophene

The electrochemical polymerisation of thiophene was first investigated by G. Tourillon and F. Garnier<sup>42</sup> and is a more straightforward and facile route than the chemical synthesis. The resulting polymer was made as a powder or film. The thickness of the polymer film could be controlled by the current. The product was conducting without further doping, since it was produced in the oxidised state during the electropolymerisation. One drawback of this method is the presence of conjugation defects resulting from  $\alpha$ - $\beta$  and  $\beta$ - $\beta$  linkages<sup>44</sup>.

As well as thiophene compounds, pyrrole and furan compounds could also be polymerised by the electrochemical method. The polypyrrole was first made by electrochemical oxidation in aqueous sulfuric acid by Dall'Olo and coworkers<sup>45,46</sup> in the late 1960's. This polymer, 'pyrrole black', was reported to be a powdery, insoluble precipitate. In 1979, Diaz and coworkers<sup>47,48</sup> re-examined the electrochemical oxidation of pyrrole and

found that a high quality, free-standing polypyrrole film, with a conductivity of up to  $100 \text{ Scm}^{-1}$ , could be made using a mixture of acetonitrile and water (99:1 by weight). It was Diaz who really established the electrochemical approach to the synthesis of conducting polymers. Since then, the electrochemical polymerisation of pyrrole has been used as the model reaction for the investigation of the mechanism of electrochemical polymerisation of conjugated heterocyclic compounds.

Unlike polypyrrole and polythiophene, polyfuran has not been extensively investigated and only a few investigations have been reported. This is partly due to the complexity of its chemistry, and the instability and poor quality of the final products of the polymerisation.

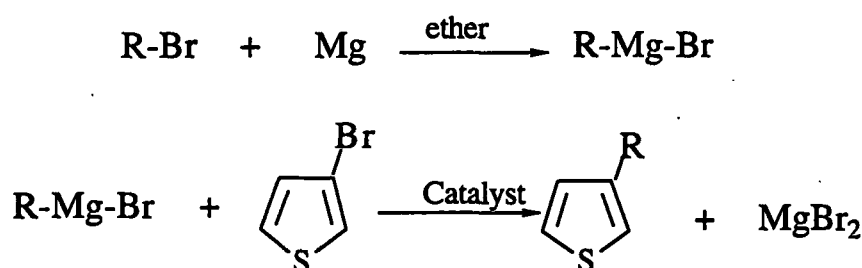
### **1.3 Structural Modification of Polythiophene**

In contrast to many other conducting polymers, polythiophene is relatively stable against attack by oxygen and moisture in both its doped and neutral states. Its structure is very versatile and offers many opportunities to modify its electrochemical and physical properties by manipulation of the monomer structure.

#### **1.3.1 Improvement of solubility**

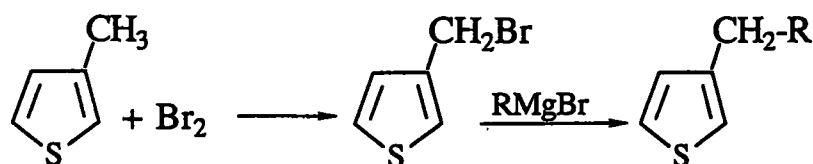
Owing to the rigidity of its conjugated backbone and the very strong interaction between the molecular chains, the parent polythiophene is insoluble in many normal organic solvents. This causes serious problems for the processing of the finished products and also prevents further characterization by classical analytical techniques. However, this problem has been solved by modifying the structure of the thiophene monomer. A series of linear alkyl groups were placed on the  $\beta$  position of a thiophene ring to form 3-alkyl thiophene derivatives. In 1986 several research groups

in Japan, France and America<sup>49,50,51</sup> reported that 3-alkylthiophenes could be polymerised by both electrochemical and pure chemical methods, and that the resulting polymer in the neutral state was soluble in some common organic solvents. The methods of chemical and electrochemical syntheses were the same as that of the parent thiophene monomer. The synthesis of the 3-alkylthiophene monomers could be carried out in two ways. One used 3-bromothiophene as the starting material, which gave the 3-alkylthiophene via a Grignard coupling with the 1-bromoalkane<sup>52</sup>. A high yield of 3-alkylthiophene product can be achieved using dichloro-1,1-bis(diphenylphosphino)propane nickel(II) (NiDPPPCl<sub>2</sub>) as a catalyst, as shown in Scheme 1-14.



Scheme 1-14 Preparation of 3-alkylthiophene

A second synthesis used the commercially available 3-methylthiophene as the starting material. This was brominated to form 3-bromomethylthiophene, followed by a Grignard coupling to give a 3-alkylthiophene<sup>53</sup> as shown in Scheme 1-15.



Scheme 1-15 An alternative preparation of 3-alkylthiophene

A number of 3-substituted alkylthiophenes with alkyl chain lengths from 1 to 20 carbons have been prepared and the corresponding polymers have been examined to study the relationship between the alkyl chain length and

the electrochemical properties of the resulting polymers. It was found that the melting point decreases monotonically as a function of the length of the alkyl chain<sup>54</sup>. Since the side chains give rise to a decrease in the interchain coupling and an increase in the molecular entropy, these derivatives can be processed into films using both their solutions and melts. The good solubility of these polymers is not only of technological importance but is also of significant scientific interest. During an investigation of the solubility and thermal melting of these polymers it was discovered that soluble 3-alkylthiophene polymers exhibit some interesting phenomena such as thermochromism and solvatochromism<sup>55</sup>, both of which are reversible. The absorption maximum in the optical absorption spectra of poly 3-hexylthiophene shifted by about 0.5 eV between room temperature and 180°C. In addition, there is a loss of optical absorption at low photon-energy, as well as an increase in the optical absorption at high photon-energy. This behaviour suggests that the energy gap between the conducting band and the valence band of the polymer would increase with increasing temperature. The analogous phenomenon of solvatochromism shows the optical absorption in poor solvents to be identical to that at low temperature in solid films and a blue shift would occur when the polymer was dissolved in a good solvent or the temperature increased. The possible explanation of this behaviour was based on evidence found using infrared and Raman spectroscopy<sup>56,57</sup>. The torsional deformation of the polymer backbone is caused by temperature-dependent side chain coiling. With increasing temperature the steric interaction within the polymer chains moves the backbone out of the planar configuration. This results in a decrease in the effective conjugation length. Thus, the blue shift would take place.

Introduction of a long alkyl chain on the thiophene ring decreases the conductivity of the resulting polymer by the decreasing both the  $\pi$ -electron

density and the charge carrier density. However, the loss of the conductivity can be compensated by stretching the solution cast film in one dimension. Hotta<sup>58</sup> reported that the conductivity of a solution processed poly(3-hexylthiophene) film increased from 27 to ca. 200 S cm<sup>-1</sup> with a stretching ratio of 5.

Compared to 3-linear alkylthiophenes, 3-branched alkylthiophenes such as 3-isopropylthiophene failed to polymerise by electrochemical methods and poly(3-isobutylthiophene) was considerably less conjugated and less conducting than its linear analog<sup>59,60</sup>. However, there is an exception. The oxidative potential and optical absorption maximum of poly(3-isoamylthiophene) were similar to that of poly(3-amylthiophene)<sup>61,62</sup>. Nevertheless, generally speaking, branched alkyl groups sharply decrease the effective conjugation of the polymer backbone and the degree of polymerisation of the monomer, possibly owing to steric factors arising from the branched groups.

### **1.3.2 Elaboration of functional groups**

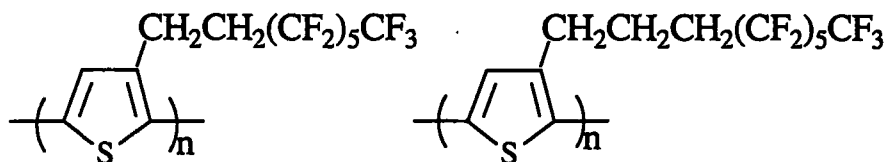
As mentioned above, 3-substituted alkyl derivatives of thiophene can be conveniently prepared by a Grignard coupling with 1-bromoalkanes. This provides a methodology for attaching a particular group to the thiophene ring, to form a derivative with extra functionality.

#### **1) Grafting on a fluoroalkyl chain**

It is known that conventional fluoropolymers possess high thermal stability, chemical inertness, have low coefficients of friction and are hydrophobic. Therefore, introduction of a fluoroalkyl group on the parent thiophene ring should lead to the formation of novel types of materials. Recently, Roncali



has successfully synthesised, by electropolymerisation<sup>63,64</sup>, polymers with pendant fluoroalkyl groups as shown in Scheme 1-16.



Scheme 1-16 Polythiophenes with pendant fluoroalkyl groups

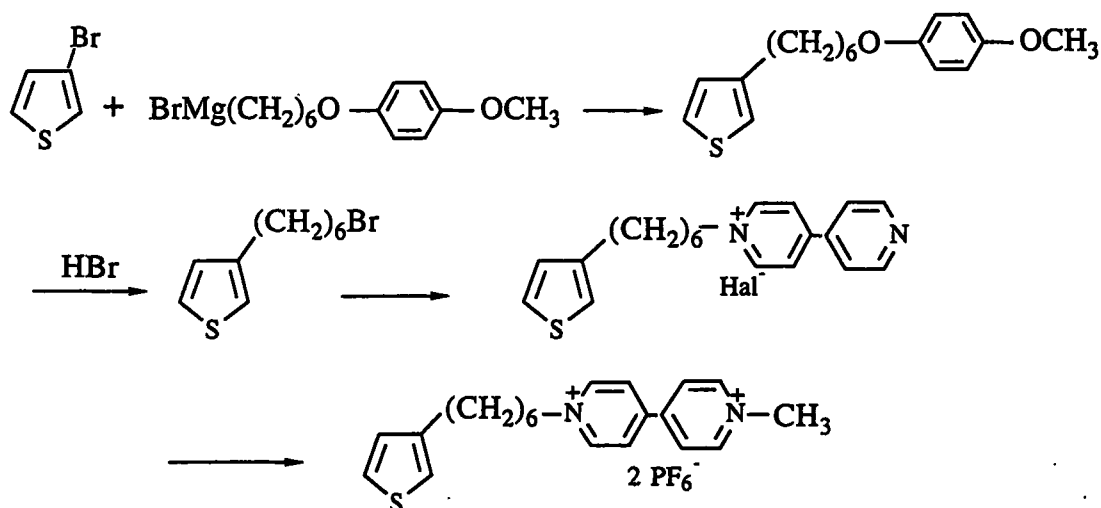
Interestingly, two or three CH<sub>2</sub> units were inserted between the thiophene ring and the fluoroalkyl units. This would neutralize the electron withdrawing effect of the fluorine atoms so that the polymerisation could be smoothly performed. It was reported that a polymer containing 50% by mass fluorine resembled an elastomeric material but with higher electroactivity than poly(3-alkylthiophenes).

## 2) Introduction of redox groups

Whilst there have been many studies of redox functionalised polypyrroles, only a few studies have been carried out on the corresponding polythiophenes, due to the high oxidation potential of thiophene compounds. This tends to destroy the electrochemical activity of any substituted redox groups on the polythiophene ring. Alternatively the high electrochemical activity of the redox group may prohibit the electropolymerisation of the corresponding monomer from taking place. Nevertheless, some successful examples have been reported by Bauerle<sup>65</sup>. The polymer with viologen or ferrocene redox groups placed on the  $\beta$  position of the thiophene ring has been synthesised and systematically investigated. The synthesis of the viologen derivative of thiophene required five steps as outlined in Scheme 1-17. The reported yield was quite low.

Conducting polymers with pendant redox groups could be used to modify an electrode surface, to show symmetrical reversible electrochemical activity

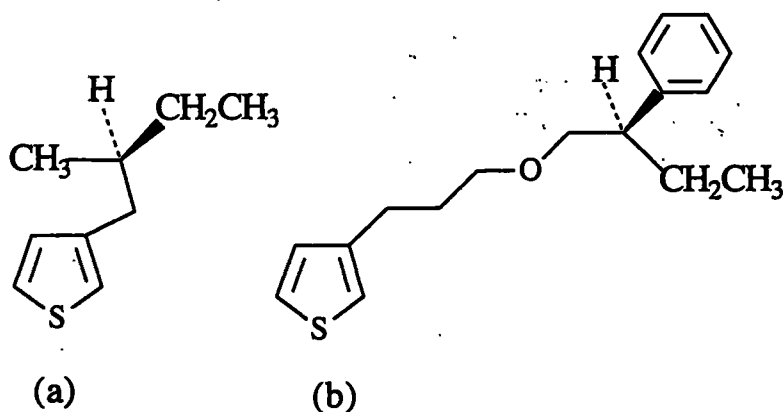
or to act as a relay in mediating electron transfer in water splitting systems and redoxenzyme chemistry.



Scheme 1-17 Preparation of a viologen derivative of thiophene

### 3) Optically active groups

Recently, a novel type of polythiophene derivative has been prepared with optically active functions such as poly[(S)-(+)-3-(2-methylbutyl)thiophene] (a)<sup>66</sup> and poly[(2S)-(+)-3-(3'-thienyl)propyl-2-phenylbutyl ether] (b)<sup>67</sup> as shown in Scheme 1-18.



Scheme 1-18 Thiophene derivatives with pendant optically active groups

Roncali reported that some chiral polythiophenes, such as (b), exhibit high specific rotation, stability and reasonable conductivity, and can stereoselectively recognize chiral anions used as doping agents during

voltammetric cycles. The stereoselective recognition of doping agents is of particular interest since these polymers have potential as materials for constructing enantioselective electrodes and membranes. Thus, chiral asymmetric compounds could be electrochemically produced by using this enantioselective electrode and enantiomeric products could be conveniently separated with this functional membrane. A key factor is to choose a suitable chiral structure which can induce high diastereoselectivity during synthesis or resolution of chiral compounds, such as ( $\pm$ )-2-phenylbutyric acid, which has been used for many years for enantiomeric excess determination of organic chiral compounds<sup>68</sup>.

#### **4) Self-doping functional groups**

Since many conjugated polymers only become conducting when they are oxidised or reduced through doping processes with cations or anions, Heeger and coworkers introduced the concept of 'self-doping'. They synthesized novel types of polythiophene derivative such as poly(3-ethanesulfonatethiophene) and poly(3-butanesulfonatethiophene). A sulphonate group in the side chain can act as the counterion upon oxidative doping. Furthermore, owing to the presence of the sulphonate group the resulting polymer is water soluble. However, the polymer cannot be directly prepared from its monomer but from its corresponding methyl suphonate ester. Firstly, the methylester is electropolymerised in the presence of a supporting electrolyte, the resulting polymer is then converted to its final form using methyl iodide in acetone.

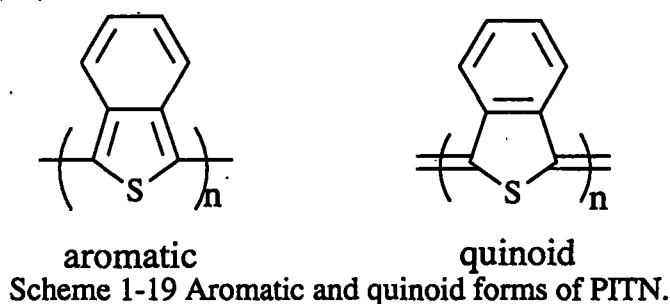
In 1989 unambiguous evidence was obtained by Havinga and Van Horssen<sup>69</sup> that 3'-propanesulfonatetrithiophene could be polymerised by electrolysis in acetonitrile without the addition of a supporting electrolyte. One possible

suggestion is that the oxidation potential of the trimer was much lower than that of the monomer, 3-propanesulfonatethiophene.

#### 1.4 Intrinsic Conducting Polymers

In 1984 Kobayashi et al prepared a fused ring derivative of polythiophene, polyisothianaphthene (PITN), via both pure chemical and electrochemical polymerisation<sup>70</sup>. PITN was found to exhibit interesting optical properties<sup>71,72</sup>. Unlike other conducting polymers, the neutral form is blue and the oxidised form is almost transparent. In situ absorption spectra of PITN recorded during the electrochemical redox show that there is an absorption maximum at 850nm (1.4eV) and an absorption onset at about 1.1eV in the neutral state, associated with the  $\pi-\pi^*$  transition (the energy gap). Compared to an energy gap of 2.1eV for the parent polythiophene, PITN has a very small energy gap (the smallest one known of any conjugated polymer). As the oxidation level is increased this absorption peak gradually disappears and new absorption peaks appear beyond the visible region towards the near IR region. This result indicates that the incorporation of the benzene ring into the thiophene structure dramatically affects the properties of the thiophene polymer. The discovery of this low band conducting polymer has prompted many studies in both chemistry and physics with the aim of creating a novel type of polymer with significant intrinsic conductivity and good nonlinear optical properties. Using quantum chemical methods, a number of theoretical studies have been undertaken to discover what exactly causes the small band gap of PITN, and what other type of compounds might have even lower energy bands. Using valence effective Hamiltonian (VEH) calculations, Bredas has suggested that since, in polyheteroaromatics, the highest occupied electronic band (HOMO), the valence band, has aromatic character and the lowest unoccupied band (LUMO), the conduction band, has quinoid character, one strategy would be

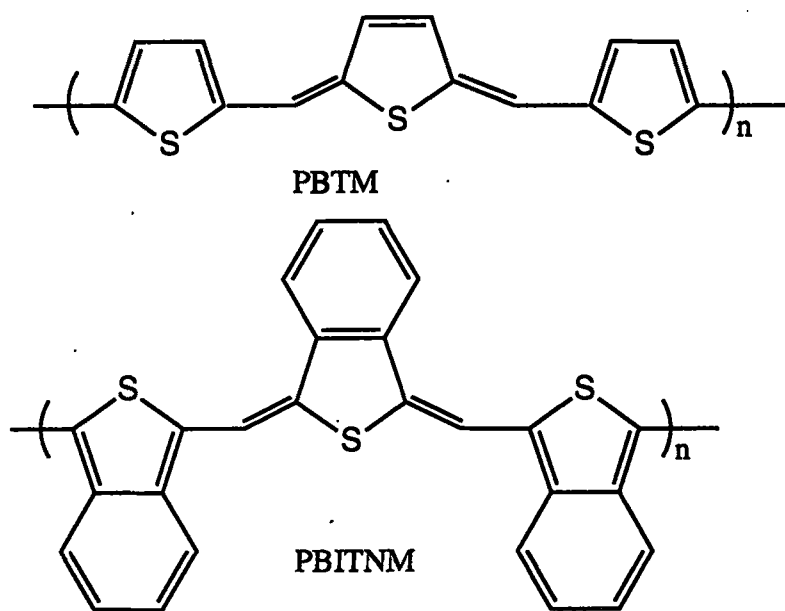
to reduce the energy gap by the addition of substituents. If they can destabilize the HOMO and stabilize the LUMO then these could force the conjugation framework towards a more quinoid-like structure<sup>73,74,75</sup>. In other words, if the most stable structure of a polymer is the quinoid form, the energy gap of the polymer would be very small. These two structures of PITN are shown in Scheme 1-19. As the quinoid contributions to the geometry increases the band gap decreases.



But some doubts have been raised by Dougherty, Kurti and Kertesz on the validity of these calculations<sup>76,77,78</sup>. They suggest that the neutral state of PITN has a quinoidal geometry rather than an aromatic geometry unlike the parent polythiophene, since the band gap value of the quinoid form is 1.16 eV compared to 0.73 eV for the aromatic form. An extra benzene ring fused onto the ITN structure would not lead to a further decrease of the energy gap and may possibly result in an increase of the band gap from 1 eV to 1.4 eV. These different conclusions may result from the different calculational methods. Bredas' calculation is based on a short chain oligomer structure of ITN, which is suggested to be aromatic. Nevertheless, the explanation of the decreasing energy gap is the same for the two calculations. It results from the increasing contribution of quinoid form of the polymer which involves bond length alternation along the backbone.

Besides the combination of a benzene ring with a thiophene ring, there are other routes to create polymers with small band gaps. Based on the above interpretation of the energy gap of heteroconjugated polymers, it was

suggested that the use of methine groups as 'bridges', to combine alternating aromatic and quinoid subunits, would form polymers with small band gaps. An example is polybithiophene-methine where half of the units are quinoid. Kertesz calculated that poly(bithiophene-methine), PBTM, would have a band gap of 1.2 eV and poly(biisothianaphthene-methine), PBITNM would have an even lower band gap of 0.7 eV. The structures of PBTM and PBITNM are shown in Scheme 1-20.

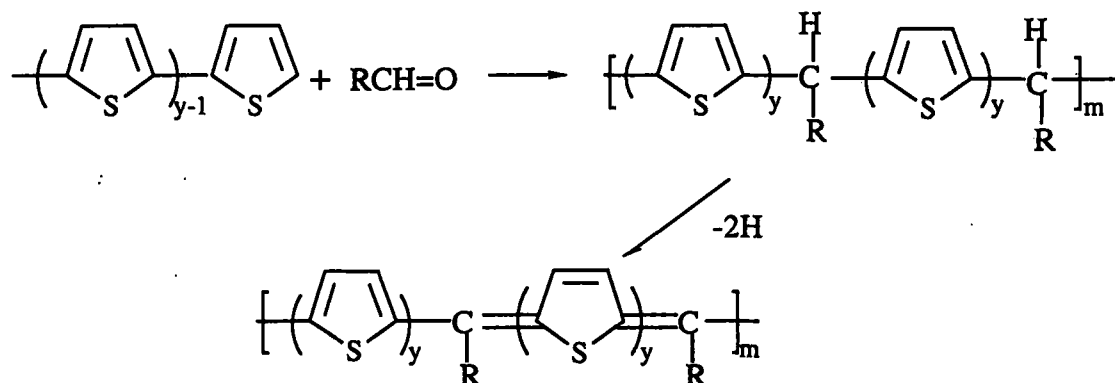


Scheme 1-20 Structures of PBTM and PBITNM

Another novel strategy to lower the band gap was to use monomers with significantly different band gaps as in poly(isothianaphthene-thiophene). The band gap of this polymer was calculated to be only 0.5 eV<sup>79</sup>. However, in the calculation there were several factors neglected which would increase the real energy gap. These include steric effects that give rise to nonplanarity, short conjugated segments, electron-electron interaction and the model correlation effects.

From a theoretical view point many interesting polymers with small band gaps have been proposed. However, not many of these have been prepared by organic chemists and no clear characterisations of the resulting polymers

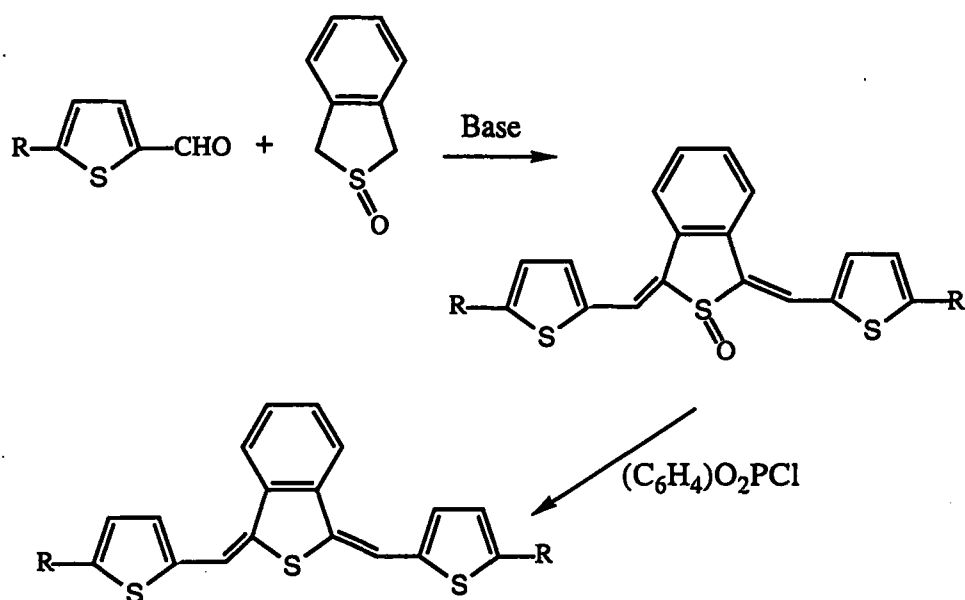
have been achieved. Jenekhe has claimed that a class of low band gap polymers with alternating aromatic and quinoid segments of thiophenes and methines has been prepared via the two step reaction shown in Scheme 1-21.



Scheme 1-21 Preparation of thiophene and methine copolymer

Firstly, precursors were synthesized by the condensation of thiophene monomers, dimers or trimers with aldehydes. The resulting precursors were then converted into conjugated polymers, with alternating aromatic and quinoid segments, by oxidative elimination of the 'bridge' hydrogens using bromine. It was reported from the optical absorption spectrum that the polymer had a band gap of 0.75 eV . However, the final product was insoluble and its optical spectrum was ambiguous. There was no mention of colour or conductivity of the product. If the conversion of the precursor to the final conjugated polymer was not complete some defects, including saturated units, may still exist in the polymer which would certainly have an effect on the band gap of the polymer.

Hanack<sup>80</sup> has developed an alternative synthesis of polymers containing alternating aromatic and quinoid type monomers. A general route is given in Scheme 1-22.



Scheme 1-22 Preparation of a methine-bridged precursor compound

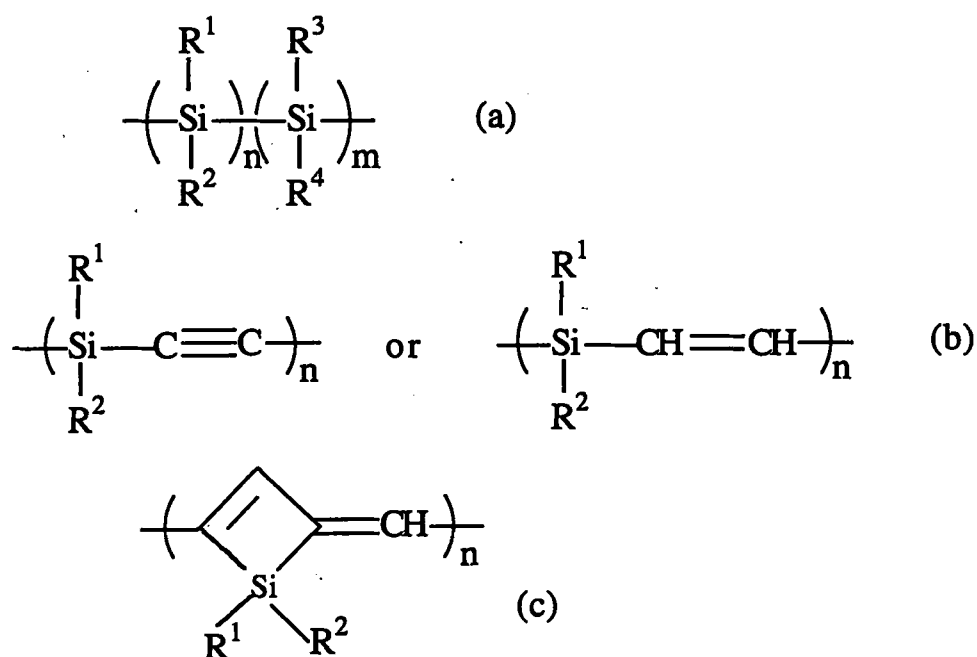
The key step involves a Knoevenagel-type condensation of 2-thiophenecarbaldehyde with 2,5-dihydrothiophene-1-oxide, and /or analogous benzo- and naphtho-annulated systems, to form the methine-bridged precursor compound. This is followed by the use of  $(\text{C}_6\text{H}_4)\text{O}_2\text{P-Cl}$ . Whilst this has been performed for small molecules, no results have been reported for the corresponding polymers.

In conclusion, the preparation of conducting polymers with a small band gap is an interesting objective, and extensive work still needs to be done to obtain a better understanding of the intrinsic conductivity of these polymers.



## 1.5 Organosilicon Polymers with Electronic and Optical Properties<sup>81,82,83</sup>

Silicon polymers, which possess potential electronic and optical activities, have only been developed over the last decade. As shown in Scheme 1-23 they include Si-Si backbone polysilanes (a), polyvinyl and/or polyethynylsilanes (b) and cyclic conjugated polysilanes (c).



Scheme 1-23 Three types of silicon polymers

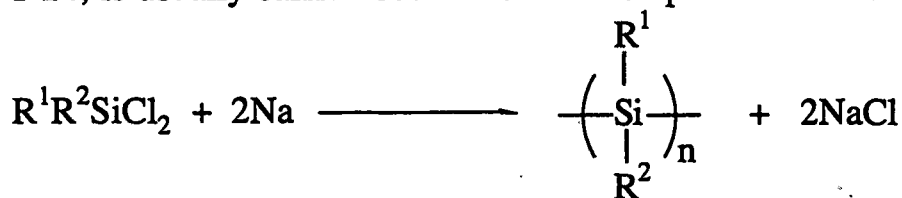
### 1.5.1 Si-Si Backbone polysilanes

The first polysilane was prepared by Kipping in the early 1920's from the reaction of diphenyldichlorosilane with sodium metal<sup>84</sup>. However, the polymer was intractable and insoluble in any organic solvent due to its high crystallinity. Thus, no further characterisation of polysilanes was carried out until the late 1970's. Re-investigation of polysilanes was initiated after the important discovery by Yajima and coworkers in Japan<sup>85,86,87</sup> that polysilanes could be converted to  $\beta$ -silicon carbide by pyrolysis. In 1981 Trujillo<sup>88</sup> synthesized a number of soluble silane homo- and copolymers

including polymethylphenyl silane. In 1980 Wesson<sup>89</sup> made copolymers containing the dimethylsilane subunits in combination with either ethylmethylsilane or methyl-n-propylsilane subunits. In 1981 West<sup>90</sup> made a copolymer of dimethylsilane in combination with methylphenylsilane. These initial studies established a base for further exploration of the potential properties of the polysilanes. Subsequently, the synthesis and characterisation of a large number of soluble homo and copolysilanes has been reported. A comprehensive review of the development of polysilanes has been published by Miller and Michl<sup>83</sup>.

### 1) Synthesis

The most well known method of preparing polysilanes is based on the Wurtz-Fittig coupling using highly reactive alkali metals such as sodium, as reported by Kipping in the 1920's. The reaction, which is shown in Scheme 1-24, is usually carried out at elevated temperature in an inert solvent.



Scheme 1-24 Preparation of polysilanes

The choice of monomers, solvents and alkali metals dramatically affects the crystallinity and molecular weight of the final products. Sodium is much more frequently used than other alkali metals such as lithium and potassium. The use of lithium often gives rise to cyclooligomerisation<sup>81,91</sup>. The use of potassium leads to the degradation of the high molecular weight linear polymers and the formation of cyclic oligomers at elevated temperature, particularly in more polar solvents such as THF<sup>92</sup>. Symmetric dialkylsilanes could be easily converted to highly crystalline peralkylpolysilanes, however, the polymers had poor solubility. The use of non-symmetric dialkylsilanes

greatly affects the nature of the polymer. Copolymerisation of phenylmethyldichlorosilane with dimethyldichlorosilane leads to polymers where the crystallinity drops sharply with the increase in the proportion of phenyl groups<sup>90</sup>. As the ratio of phenyl and methyl groups approaches one the polymer is almost amorphous and highly soluble in organic solvents at room temperature. It was also noted that many of the polymerisation reactions were strongly solvent dependent. Miller reported that the use of diglyme and toluene as cosolvents resulted in an improvement of the overall polymer yield and changed the molecular weight distribution<sup>93</sup>.

More recently, alternative procedures have been developed to prepare polysilanes. Examples are; firstly the preparation of low molecular weight polysilane derivatives from substituted silanes using catalytic quantities of early-transition-metal complexes of titanium and zirconium<sup>94,95,96</sup>; secondly the utilisation of ultrasonic agitation to obtain monodisperse high molecular weight polymers<sup>97</sup>; and finally functionalisation of polysilanes by addition of triflate groups to generate alkoxy-substituted polysilane derivatives<sup>98</sup>.

## **2) Electronic and optical properties of polysilanes**

One of main interests of polysilanes has been the unusually low electronic excitation energy. All soluble high molecular weight polysilane derivatives possess a characteristic long wavelength absorption between 300 and 400nm<sup>99</sup>. The absorption wavelength is closely associated with the polymer chain length and the nature of the substituent groups on silicon. Generally, the absorption maximum wavelength increases with the increasing polymer chain length. Aromatic substituents directly linked to the silicon cause a red shift in the position of the absorption maximum. This significantly differs from that of conventional saturated carbon polymers where the optical

absorption maximum is below 200nm. It was also found that many polysilanes show a strong thermochromic behaviour<sup>100,101</sup>. The absorption maximum shifts gradually and reversibly to longer wavelengths as the temperature decreases. Such low energy absorptions of polysilanes suggest that sigma conjugation and sigma delocalisation are important in the electronic structure of polysilanes. This is similar to the pi-electron system of a carbon based polyene chain with alternating double bonds. As a result of this sigma delocalisation, the electrochemical properties of many polysilanes have been examined. It has been reported that polysilanes can be converted into semiconductors by treatment with oxidizing agents such as SbF<sub>5</sub>, AsF<sub>5</sub> and I<sub>2</sub>. However, the mechanism of conduction is somewhat different from that of polyenes. The conformation of a polyene chain is characterised by alternating short (double) and long (single) bond distances. Geometric adjustment in the excited state enables the formation of polarons and solitons etc, along the polymer chains. In a polysilane chain the alternation of the strong and weak resonance state is dependent on the alternation of bonds and atoms rather than the alternation of short and long bonds, such that the formation of analogous species in the polysilane chains will not be the same<sup>102</sup>. One suggestion is that oxidation produces a cation-radical, analogous to a 'hole' in elemental silicon, and this positive charge is mobile along the polysilane chain<sup>102</sup>. However, such oxidation states are very unstable and react rapidly with air and moisture. The doped polysilanes are of thus more scientific than practical interest.

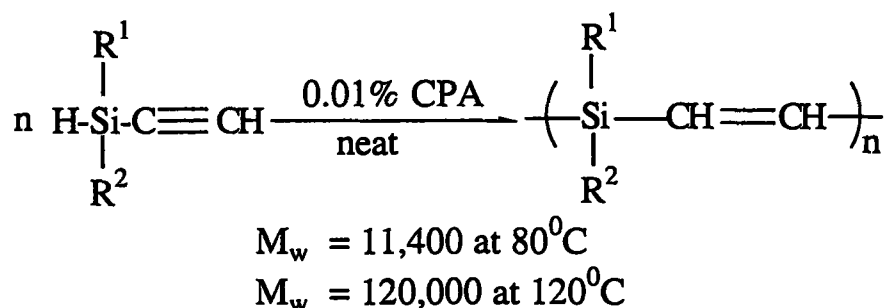
As well as the behaviour mentioned above, polysilanes are photoactive owing to an extremely strong absorption in the UV region. Thus, photoscission of polysilanes takes place under irradiation leading to the formation of silyl radicals. This could have applications in the polymerisation of olefins using polysilanes as photoinitiators. West and

coworkers were the first to propose this route and successfully polymerised styrene and methylmethacrylate by using a polysilane as a photoinitiator<sup>103,104</sup>. The photoactivity of polysilanes also makes them suitable for many potential lithographic application such as photoresists<sup>105</sup>.

More recently, there have been a number of studies on the nonlinear optical (NLO) properties of polysilanes owing to their intrinsically large nonlinear susceptibilities and rapid response times<sup>106,107</sup>. They are particularly interesting since they are thermally and oxidatively stable and very soluble in common organic solvents. These properties make them more useful than other delocalised pi-conjugated organic polymers. This combination of electronic and physical properties indicates that polysilanes are an attractive new class of nonlinear optical materials, although there is still a great deal of work to be done.

### **1.5.2 Si-C backbone polysilanes**

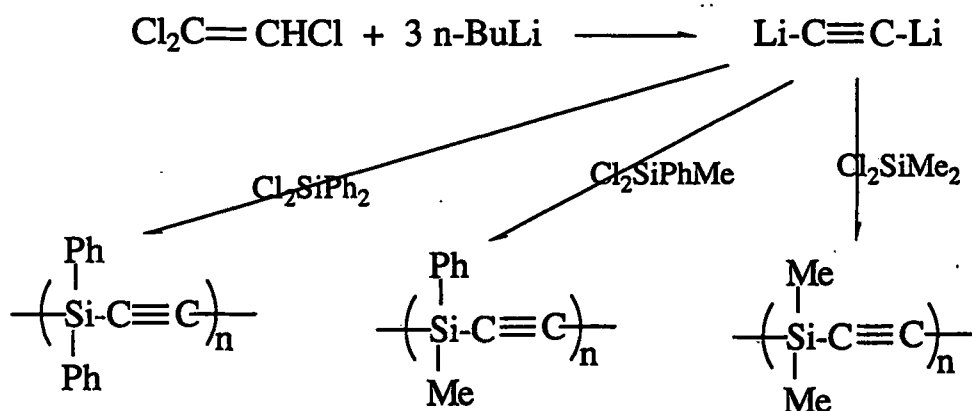
Developments in Si-Si backbone polysilanes and conjugated carbon backbone polymers has led to the combination of silyl units and pi-electron systems into the same polymer, in the hope that they will complement each other in electronic, optical and physical properties. The pioneering work of Ishikawa, Corriu and Barton have led to a range of polysilyl-olefins, polysilyl-acetylenes and polysilyl-aromatic compounds<sup>108-112</sup>. One of the procedures for the synthesis of polysilyl-olefins by the hydrosilylation of acetylene, catalysed with chloroplatinic acid (CPA), is shown in Scheme 1-25.



Scheme 1-25 Preparation of polysilyl-olefins

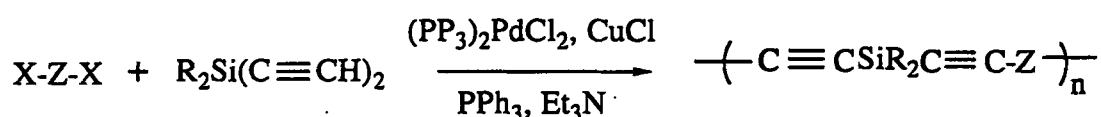
The polymerisation of ethynylsilyl hydrides can be easily carried out either neat or in THF to achieve very high yields of more than 90%. The resulting polymers are soluble in a variety of organic solvents. The molecular weight of the polymers depends on the reaction temperature.

Silicon-acetylene polymers were first made in the early 1960's by Korshak<sup>113</sup> by the reaction of the acetylenic diGrignard reagents with dialkylsilanes. The polymers were reported as black resins with low molecular weight which seemed to have very little value. However, recently, alternative processes have been found to prepare these polymers. One satisfactory method is the reaction of trichloroethylene with 3 equivalents of n-butyllithium to form dilithioacetylene. This is followed by quenching with dichlorosilanes, to obtain the desired silicon-acetylene polymers with high molecular weight, as shown in Scheme 1-26.



Scheme 1-26 Preparation of polysilyl-acetylene

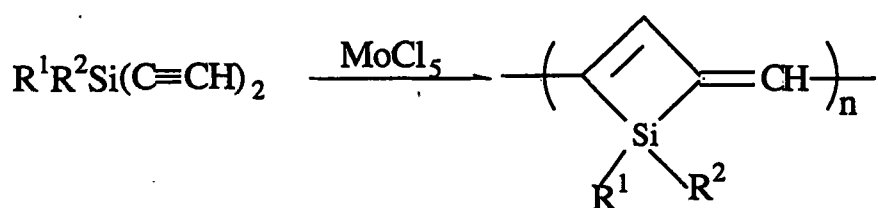
Corriu and coworkers<sup>114</sup> reported that a range of polyalkynylsilanes had been made by a palladium-catalyzed coupling reaction between diethynyldiphenylsilane and dihaloarenes (X = Br, I; Z = (hetero)aromatic groups):



The conductivity of these polymers was found to be higher than that of Si-Si backbone polysilanes. However, the UV absorption characteristics remained the same.

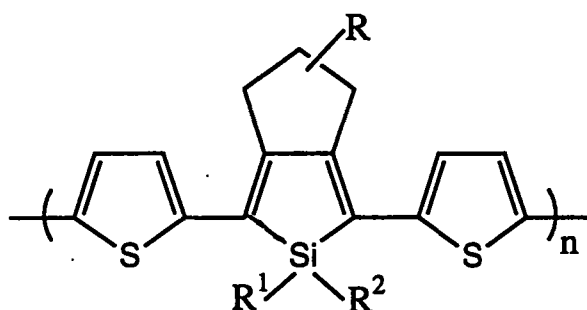
Silylene and thienylene units have also been combined by the reaction of thiophene oligomers with n-butyllithium, followed by condensation with dichlorosilanes and termination with methyllithium. This affords poly(2,5-silylthiophene) with one to five thienylene and up to six silylene units in the polymer chain<sup>115</sup>. The resulting polymers are soluble in common organic solvents and can be cast to give insulating films. After doping with NOBF<sub>4</sub> the polymers become conducting but have much lower conductivity than the parent polythiophene. There was no mention of the stability of the polymers in air and moisture.

It is surprising that, except for two examples, little work has been reported on the cyclic polysilanes. The first was a type of polydiethynylsilane consisting of units of four-membered rings alternately connected to CH and SiR<sub>2</sub> units as illustrated in Scheme 1-27<sup>116</sup>.



Scheme 1-27 Preparation of polydiethynylsilanes

Diethynylsilane is directly polymerized by a  $\text{MoCl}_5$  catalyst. The conformation of the polymer can be regarded as possessing an almost degenerate ground state, and the polymer exhibits a strong ultrafast nonlinear optical response. However, the polymer has a relatively short average conjugation length, resulting in the absence of a thermochromic effect and low conductivity. The second example is a copolymer consisting of a thiophene-silole-thiophene skeleton as shown in Scheme 1-28<sup>117</sup>.



Scheme 1-28 Structure of thiophene-silole polymer.

The aim of the work was to improve the perturbation in the  $\pi$ -electron system by introduction of an electron-deficient (electron-accepting) silole ring into the electron-rich polythiophene chain. It was found that the combination of thiophene and silole ring causes large red shifts of the electronic absorption compared with the parent polythiophene. The conductivity of the polymer was very low, about  $0.001 \text{ Scm}^{-1}$ , possibly due to the limited degree of polymerisation.

## 1.6 Objectives and Scope of The Present Work

Polyisothianaphthene has the lowest energy gap of all the conducting homopolymers and shows a very interesting colour change from blue in the neutral state to almost transparent in the oxidised state. This suggests applications in electrochromic display devices and others. On the other hand, this polymer is also attracting attention from theoretical physicists and chemists. The hope is to develop a new class of conjugated polymers, with



high intrinsic conductivity, by structure modification of the parent conducting polymers.

Very few reports have been concerned with five-membered silole polymers, although Si-Si backbone polysilanes are being extensively studied. Thus, a second aim is to prepare polysilole compounds and test their properties. Based on these aims the objectives of this work may be summarised as:

- 1) To prepare a range of derivatives of the parent isothianaphthene with methyl, methoxy and benzene groups.
- 2) To examine the effects of substituents on electrochemical and pure chemical polymerisation of the resulting monomers, and the conductivity of the corresponding polymers, as well as their intrinsic energy band gaps.
- 3) To explore the physical and electrochemical properties of the resulting polymers with UV/Vis/near IR, FTIR, NMR, X-ray powder diffraction and Cyclic voltammetry.
- 4) To verify the structure of many intermediate products produced during pure chemical and electrochemical polymerisation of isothianaphthene and its derivatives using GC, HPLC and Mass spectrometers.
- 5) To prepare a range of derivatives of silacyclopentadiene with methyl and phenyl and chlorine functionalised groups, and to convert these five-membered silole compounds to polymers by electrochemical and pure chemical polymerisation.

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# Chapter Two

## Synthesis of Sulphur and Silicon Containing Monomers

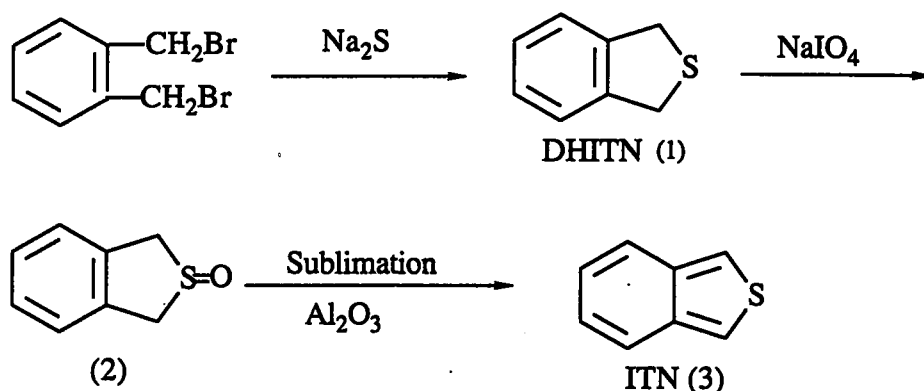
### 2.1 Synthesis of Isothianaphthene Derivatives

Modification of the thiophene ring prior to polymerisation has attracted the attention of many scientists. Attaching a long chain alkyl group to the  $\beta$  position of thiophene has been used to improve the solubility of its polymers in organic solvents and make them more processible. However, owing to the quite high energy band gap of the original polythiophene, its intrinsic conductivity is very low and the polymer needs heavy doping to obtain good conduction. Unfortunately, the mechanical strength of the conducting polymer is lost when it is heavily doped. To overcome this problem a number of conjugated polymers with relatively low energy band gaps have been made. The first successful attempt was carried out by Wudl, Kobayashi and Heeger<sup>1,2,3</sup>. By using isothianaphthene as the monomer a polymer was formed which has the lowest band gap (1.1eV) ever reported.

It has been suggested<sup>4</sup> that substituents such as methyl, methoxy and nitrile at positions 5 and 6 of the isothianaphthene ring are not likely to affect the energy band gap. However, few experiments have been reported which examine this suggestion. Therefore, we prepared a range of novel derivatives of isothianaphthene and investigated the effect of substituents on conductivity. This section describes the synthesis of isothianaphthene and its derivatives.

### 2.1.1 Isothianaphthene (ITN)

It was found that the best route to make isothianaphthene (3) was via a three-stage process, as shown in Scheme 2-1<sup>5,6,7,8</sup>.



Scheme 2-1 Preparation of isothianaphthene(ITN).

1,3-dihydrobenzo-[c]-thiophene (DHITN) (1) was prepared by a modification of the method of King<sup>8</sup>. In the original preparation  $\alpha,\alpha'$ -dibromo-o-xylene was extracted using a Soxhlet, into a refluxing solution of sodium sulfide nonahydrate in a mixture of ethyl alcohol and water. However, the yield of the product was low, below 30%, due to the high temperature of the reaction. In this work finely powdered  $\alpha,\alpha'$ -dibromo-o-xylene was slowly added in very small portions to the mixture of sodium sulfide nonahydrate in ethanol (99%) under the protection of nitrogen. The temperature of the reaction was carefully controlled at about 50 - 55°C to favour the cyclisation rather than the intermolecular polymerisation and to avoid the further reaction of the product. The yield of the product was increased to 55-60%.

Due to the high sensitivity of DHITN (1) to light and air the preparation of 1,3-dihydrobenzo-[c]-thiophene-2-oxide was carried out immediately.

DHITN (1) was added to a stirred solution of sodium periodate in 50% aqueous methanol. The oxidation took place very rapidly to form the sulfur oxide (2). It was found that the success of the preparation of (2) depended

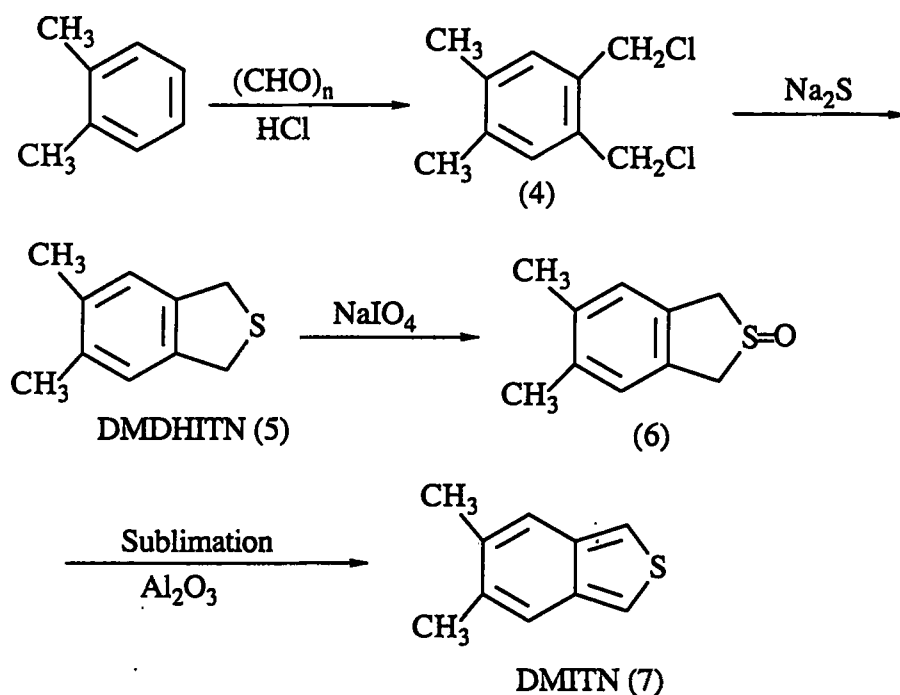
on how well the temperature was controlled. The reaction flask should be immersed in a water bath maintained at 40-45°C. If DHITN was added too quickly, the reaction temperature rose sharply leading to the overoxidation of DHITN (1) to the dioxide and ring opening, so that the yield of the desired sulfur oxide (2) was reduced.

The isothianaphthene monomer (3) was synthesized by a modification of the method of Cava et al<sup>7</sup>. A mixture of 1,3-dihydroisothianaphthene-2-oxide (2) and neutral alumina was heated under reduced pressure in a sublimation apparatus to give isothianaphthene (3) as a pure white crystalline solid. The product should be immediately stored under dry nitrogen in a freezer since it is rather unstable and becomes black very quickly when exposed to the atmosphere. This is especially true if it is dissolved in an aprotic solvent such as acetonitrile, dichloromethane or chloroform. Thus, the precise <sup>1</sup>H and <sup>13</sup>C NMR spectra could not be obtained when deuterated chloroform was used as the solvent. Interestingly, we found that when deuterated benzene was used in place of chloroform the ITN solution became black relatively slowly, so that the <sup>1</sup>H and <sup>13</sup>C NMR spectra of ITN could be obtained. In the <sup>1</sup>H NMR spectrum a singlet for two protons on C<sub>1</sub> and C<sub>3</sub> occurs at 7.18ppm. Two sets of multiplets centred at about 6.87 and 7.38 ppm can be seen for the four protons on the benzene ring.

The structure and purity of compounds (1), (2) and (3) were all verified by <sup>1</sup>H NMR, <sup>13</sup>C NMR, Mass and FT-IR spectra which are listed in the experimental section.

### **2.1.2 5,6-Dimethylisothianaphthene (DMITN)**

Having successfully made ITN via the method of Cava et al, an  $\alpha,\alpha'$ -dihalo-o-xylene was chosen as the key intermediate for preparation of DMITN, as shown in Scheme 2-2.



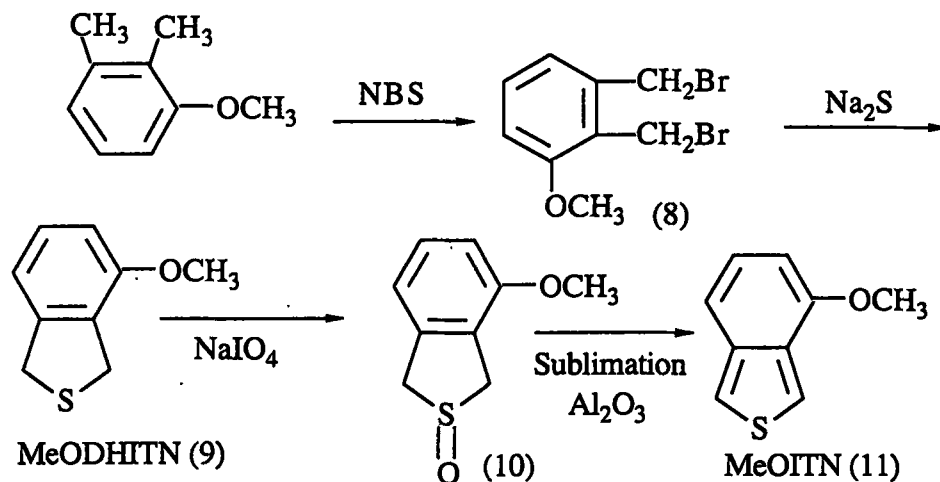
Scheme 2-2 Preparation of 5,6-dimethylbenzo-[c]-thiophene(DMITN).

1,2-Di(chloromethyl)-4,5-dimethylbenzene (4) was prepared by a modification of the method of Wood et al<sup>9,10</sup>. o-Xylene was used as the starting material, two chloromethyl groups could be directly introduced, by the action of paraformaldehyde and concentrated hydrogen chloride. It was noted that the reaction time is critical, the optimum being reflux for about 22 hours. If the time exceeded 24 hours the product further reacted with paraformaldehyde and HCl to form by-products. The rest of the synthesis was similar to that of ITN except that it was found that DMDHITN (5) was much more stable to oxidation than DHITN. This may be because of the electron donating methyl substituents at positions 5 and 6. Thus the reaction was carried out at the higher temperature of 60°C to 70°C. Again the final compound, DMITN, was founded to be more stable than the parent isothianaphthene (3).

The structure and purity of compounds (4), (5), (6) and (7) were confirmed by FT-IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR and Mass spectra as listed in the experimental section.

### 2.1.3 4-Methoxyisothianaphthene (MeOITN)

To prepare this novel compound we chose 2,3-dimethylanisole as the starting material which, upon bromination using N-bromosuccinimide in carbon tetrachloride gave 2,3-bis(bromomethyl)-anisole (8)<sup>11</sup> which could be cyclised to give the final product (11) as outlined in Scheme 2-3.



Scheme 2-3 Preparation of 4-methoxybenzo-[c]-thiophene(MeOITN).

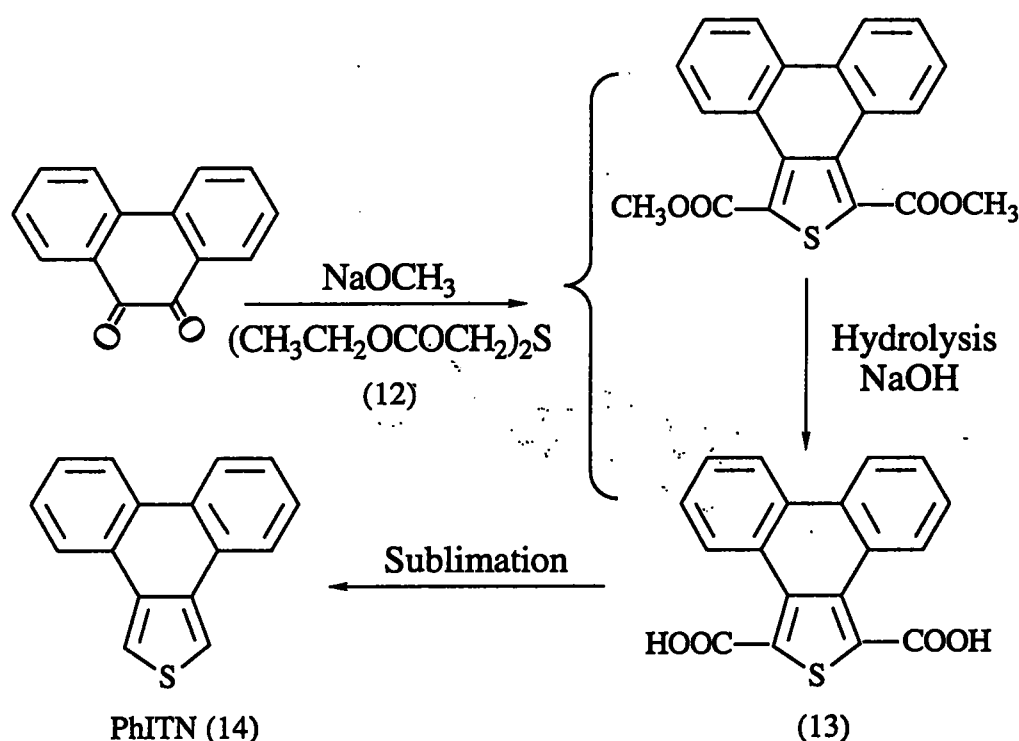
The bromination of 2,3-dimethylanisole with N-bromosuccinimide in carbon tetrachloride was performed using light. It was found that irradiation using a lamp was essential to lead to the formation of 2,3-bis(bromomethyl)-anisole (8). Without this irradiation, the reaction gave a mixture of mono and dibromo, by-products which were difficult to separate. When a radical initiator, such as benzoyl peroxide, was used the bromination occurred very rapidly, in less than two hours.

The rest of the synthesis was similar to that of ITN except that, as with DMDHITN (5), MeODHITN (9) is more stable to air and light than DHITN, so that the oxidation process took much longer time to complete and the reaction temperature needed to be slightly higher.

The structure and purity of these compounds were verified by FT-IR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, Mass spectra and the elemental analysis as listed in the experimental section.

#### 2.1.4 Phenanthrenethiophene (PhITN)

If Polyisothianaphthene (PITN) has the smallest energy gap ( $E_g = 1.0\text{eV}$ ) known, it may be possible to further reduce the band gap by introducing polycyclic aromatic rings onto the original thiophene structure. To examine this hypothesis phenanthrenethiophene was selected as a monomer. The preparation of this compound is different to that of the other isothianaphthenes made in this work. The approach taken for the synthesis of phenanthrenethiophene (14) is outlined in Scheme 2-4.



Scheme 2-4 Preparation of phenanthrenethiophene.

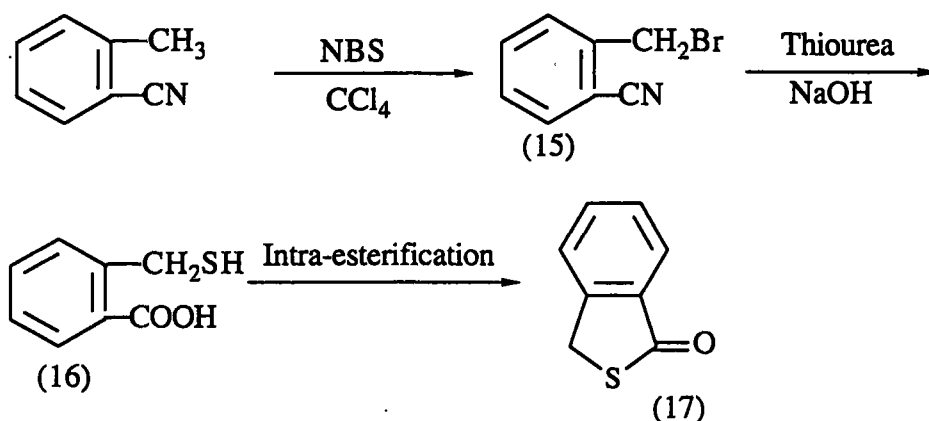


The preparation of phenanthrenethiophene dicarboxylic acid (13)<sup>12</sup> was achieved by the reaction of phenanthrenequinone and thiodiglycolic ester in the presence of sodium methoxide. However, contrary to reference 12, it was difficult to purify the crude product by recrystallisation from ethanol. The NMR and Mass spectra of the crude product indicated that it was a mixture consisting of phenanthrenethiophene dicarboxylic acid and its ester. Since the acid is the desired product the mixture was hydrolysed with base to give only the acid.

It was reported<sup>12</sup> that heating the carboxylic acid over a flame under nitrogen led to loss of carbon dioxide and formation of PhITN (14). We found it was difficult to control the reaction temperature using this method and a black, unknown, product was formed, such that the yield of the desired product was very low. An alternative procedure was therefore used to prepare this product. Sublimation of phenanthrenethiophene dicarboxylic acid (13) gave a crude product which was purified by flash column chromatography using silica gel with diethyl ether. It was found that this monomer, PhITN, is very stable to air and light, unlike ITN and DMITN, which needed to be stored under nitrogen in a freezer. The structure and purity of PhITN were confirmed by FT-IR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, Mass spectra and elemental analyses as listed in the experimental section.

### 2.1.5 Thiophthalide

Due to the sensitivity of the ITN monomer to air and light we proposed an alternative way of making polyITN from a thiophthalide monomer which is more stable to air and light. This monomer was prepared via a three step route as summarised in Scheme 2-5.



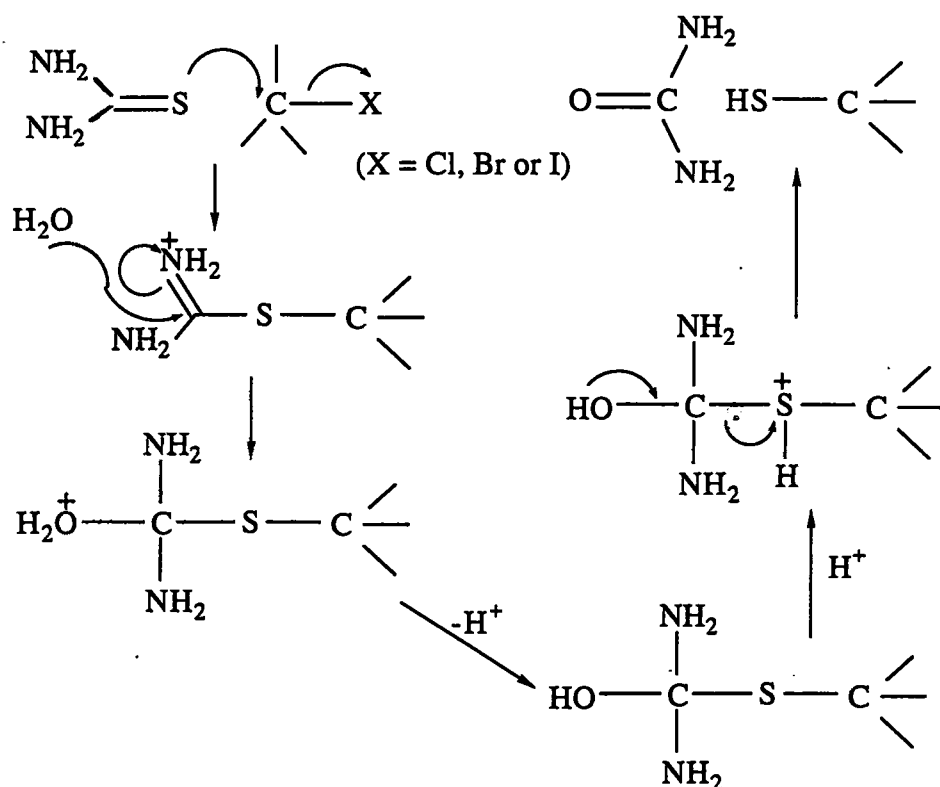
Scheme 2-5 Preparation of thiophthalide.

$\alpha$ -Bromo-o-tolunitrile (15) was prepared by bromination of o-tolunitrile with N-bromosuccinimide in carbon tetrachloride under light irradiation. The reaction was completed very rapidly within 4 hours to give a white crystalline solid in excess of 80% yield.

The next step in the synthetic scheme was the conversion of the methylene halide ( $-\text{CH}_2\text{-Br}$ ) and the cyanide ( $-\text{CN}$ ) groups of  $\alpha$ -bromo-o-tolunitrile (15) into a methylene thiol ( $-\text{CH}_2\text{-SH}$ ) and carboxylic acid ( $-\text{COOH}$ ) groups respectively.  $\alpha$ -Bromo-o-tolunitrile (15) was reacted with thiourea in water in the presence of base. The proposed mechanism for the formation of the thiol is given in Scheme 2-5a. At the same reaction the cyanide group was readily hydrolysed to give a carboxylic acid group.

In the final stage the thiol acid was intramolecularly esterified in toluene in the presence of a catalyst, toluene-4-sulfonic acid monohydrate to give the final product, thiophthalide (17).

The structure and purity of these compounds were confirmed by FT-IR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, Mass spectra and elemental analyses which are listed in the experimental section.



Scheme 2-5a A reaction mechanism for the formation of thiol

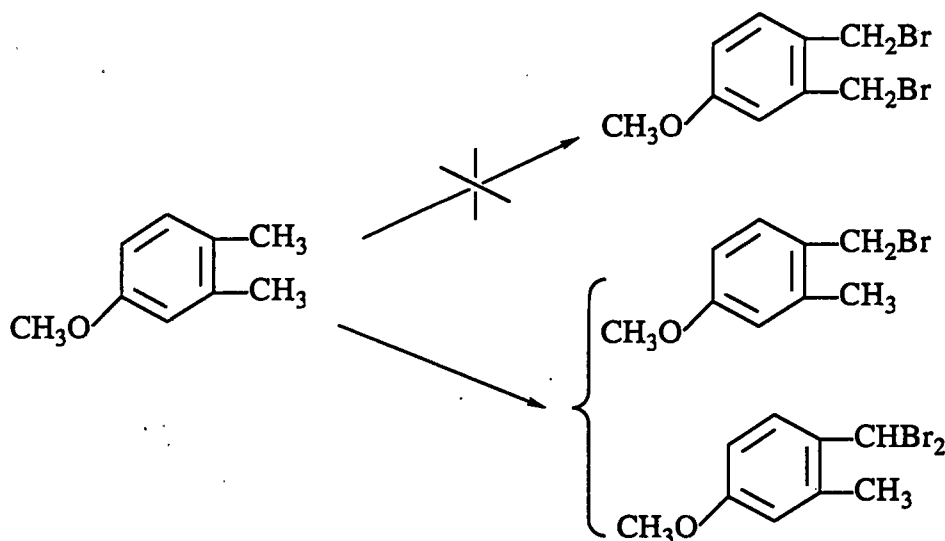
## 2.1.6 Attempts to prepare other derivatives of isothianaphthene

### 1) 5-Methoxyisothianaphthene

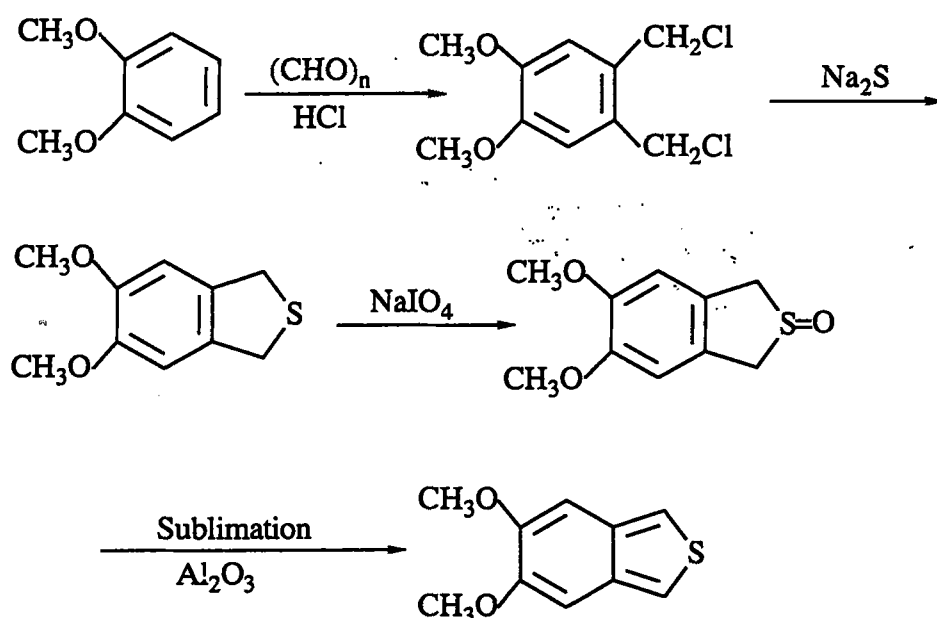
Following the successful preparation of 4-methoxy isothianaphthene we tried to make a derivative of isothianaphthene with a methoxy substituent in the 5 position. This would enable us to compare the effect of substituents at different positions of the benzene ring on the electropolymerisation and the physical properties of the resulting polymers.

It was expected that the bromination of 3,4-dimethylanisole with N-bromosuccinimide would lead to the formation of 3,4-bis(bromomethyl) anisole. Unfortunately, the bromination only took place on the methyl group at position 4 to form mono and dibromo by-products. The reaction was repeated using different conditions, such as irradiation or using benzoyl peroxide as an initiator, however, no bromination was observed on the

methyl group at position 3. One reason for this behaviour may be that the electron donating methoxy group makes the methyl group at position 4 more readily attacked by the active bromine agent.



## 2) 5,6-Dimethoxyisothianaphthene



By mimicking the procedure used to prepare 5,6-dimethyl-isothianaphthene we tried to produce 5,6-dimethoxyisothianaphthene via the condensation of veratrol with paraformaldehyde and  $\text{HCl}$ . Unfortunately, the yield of the

first step was very low, less than 10%. It was found that the paraformaldehyde was precipitated from the HCl solution when veratrol was added giving a three phase system. As the reaction progressed the mixture became grey and then deep black. It is possible that an oxidative trimerization of veratrol takes place in the presence of concentrated HCl. There is some evidence in the literature that veratrol could be trimerised using 70% sulfuric acid with chloranil<sup>13,14</sup>. THF was used as an alternative solvent to avoid the precipitation of paraformaldehyde, however, the THF was cleaved by the HCl.

## **2.2 Synthesis of Silicon Containing Monomers**

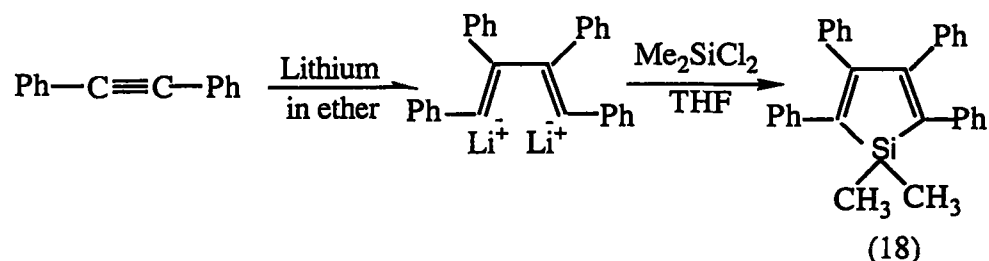
Recently, a 1-silacyclopenta-2,4-diene unit has been combined with a thiophene unit to form a conducting polymer consisting of a thiophene-silole-thiophene skeleton. The resulting polymer has a larger red shift in the electron absorption spectrum than the parent polythiophene<sup>15</sup>. However, very few reports have been published on the preparation of polysiloles. This is because the synthesis of silacyclopentadienes often involves relatively complicated and lengthy procedures, or the synthetic routes are restricted to a specific compounds<sup>16-18</sup>. In this section we detail the preparation of silacyclopentadiene compounds and discuss attempts to synthesis some 2,5-functionalised silacyclopentadiene compounds.

### **2.2.1 Synthesis of silacyclopentadienes**

#### **2.2.1.1 1,1-Dimethyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene (TPSCP)**

2,3,4,5-tetraphenyl-1-silacyclopentadienes are very easily prepared by the reaction of diphenyl acetylene with lithium in THF or diethyl ether to form 1,4-dilithio-tetraphenylbutadiene, followed by cyclisation of the resulting

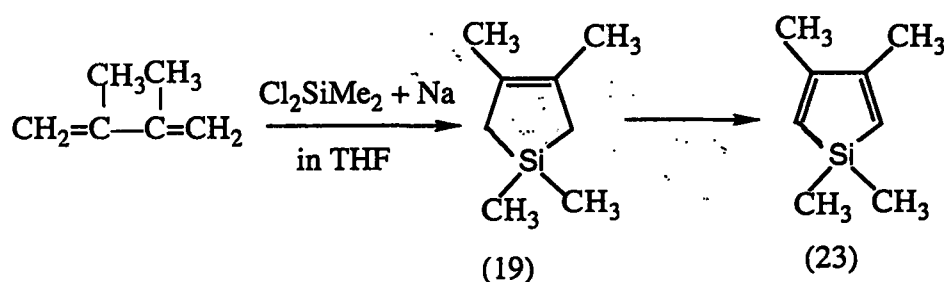
dilithio-dianion with a corresponding dihalosilane. The synthetic route can be outlined as shown in Scheme 2-6<sup>16,17</sup>. The yellow-green final product was obtained in 70% yield.



Scheme 2-6 Preparation of 1,1-dimethyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene.

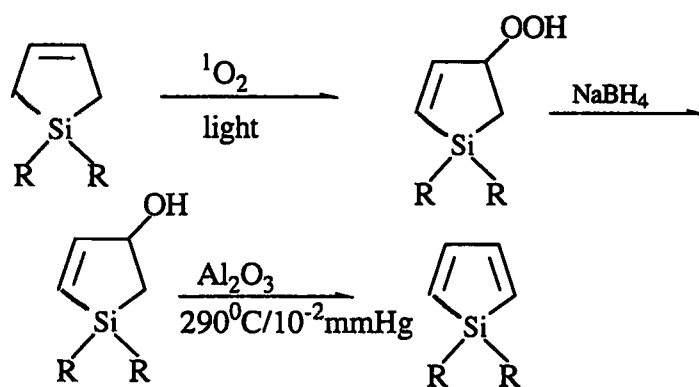
### 2.2.1.2 1,1,3,4-Tetramethyl-1-silacyclopentadiene (TMSCPD)

To our knowledge only three procedures for the preparation of TMSCPD (23) have been reported<sup>19,20,21</sup>. All of them started with the preparation of sila-3-cyclopentene by cyclisation of 2,3-dimethylbutadiene with dimethyldichlorosilane in the presence of an alkali metal to give 1,1,3,4-tetramethyl-1-sila-3-cyclopentene (19). The yield of the silacyclopentene was high (55%) when sodium was used and THF was chosen as the solvent.



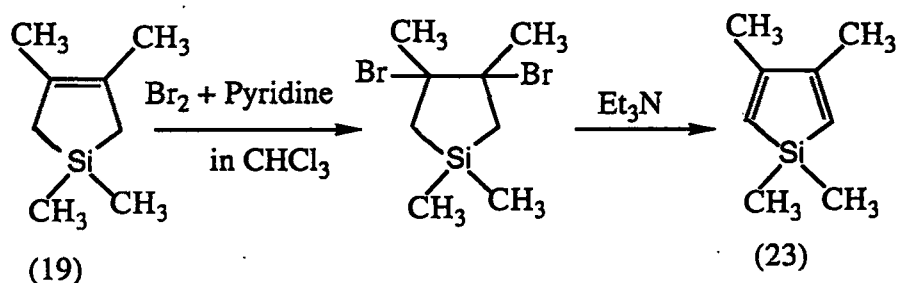
Scheme 2-7 Preparation of 1,1,3,4-tetramethyl-1-sila-3-cyclopentene

However, the conversion of the silacyclopentene (19) to the corresponding silacyclopentadiene (23) is a relatively difficult process. The first method, reported in 1981, makes use of photoirradiation using a quartz/halogen lamp. The reaction route is outlined below.



The aim was to convert the sila-3-cyclopentene to a hydroperoxide via an ene reaction. The resulting hydroperoxide was then treated with  $\text{NaBH}_4$  to give a silacyclopent-4-ene-3-ol. Finally the alcohol was treated with  $\text{Al}_2\text{O}_3$  in vacuo ( $10^{-2}$  mmHg) and at a high temperature ( $290^\circ\text{C}$ ) to form a silacyclopentadiene. The synthesis involves the use of special equipment for generating singlet oxygen and in our hands the reaction was not always regioselective. This coupled with a low yield meant that we could not synthesise the quantities required for polymerisation. Thus, it was decided to examine other routes.

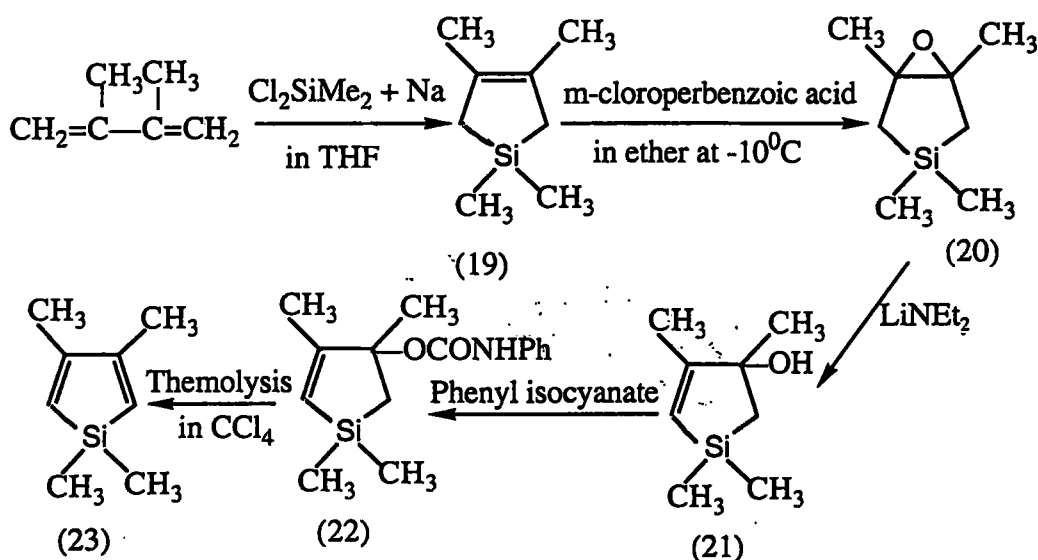
One report<sup>21</sup> claims that reaction of 1,1,3,4-tetramethyl-1-sila-3-cyclopentene with bromine, in the presence of pyridine as a catalyst, gives 3,4-dibromo-1,1,3,4-tetramethyl-1-silacyclopentane. This can then be dehydrobrominated with triethylamine to give the required product.



However, when we followed this procedure, the product of bromination was a complex mixture and the dibromo intermediate could not be isolated. The

main product of dehydrobromination seemed to be a dimer formed from the Diels-Alder reaction of TMSCPD (23).

Fortunately, an alternative method has been developed to prepare the target compound. Essentially this method is an adaption of the first procedure which involves converting the silacyclopentene to the alcohol, then to the silacyclopentadiene. The first step is the epoxidation of the silacyclopentene. The resulting epoxide undergoes a base-promoted rearrangement with lithium diethylamide, which is a poor nucleophile but a strong base, thus giving the desired allylic alcohol<sup>22</sup>. The alcohol was further reacted with phenyl isocyanate to form the carbamate of the silacyclopent-4-ene-3-ol which would lead to the formation of the expected silole on thermolysis. The details of the improved synthesis of the silole are summarised in Scheme 2-8.

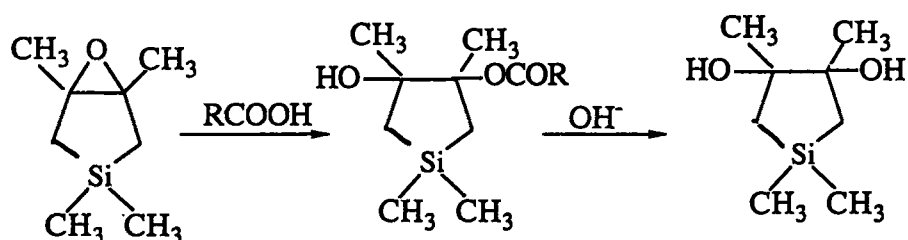


Scheme 2-8 Preparation of 1,1,3,4-tetramethyl-1-silacyclopentadiene.

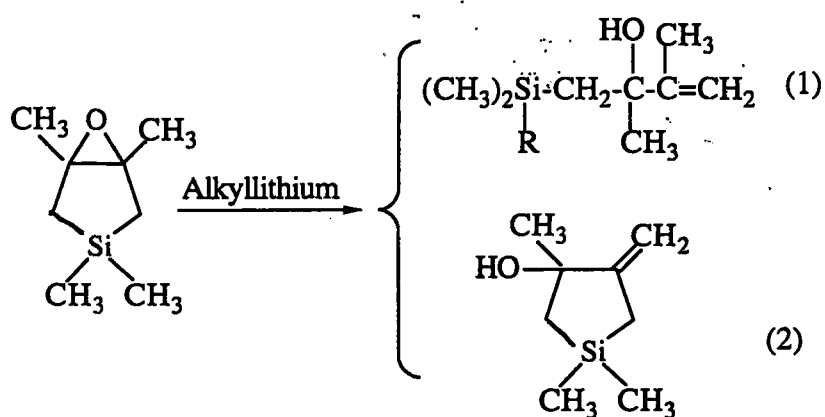
The cyclisation of 2,3-dimethylbutadiene with dimethyldichlorosilane proceeded in 55% yield. The residue was made up of a mixture of cyclic dimers and linear oligomers. It was found that if the reaction temperature increased cyclic dimers and linear oligomers predominated.



In the epoxidation of the silacyclopentene (19) the reaction time and temperature needs to be strictly controlled. A longer time and higher temperature leads to further reaction. The required product may decompose in the acidic solution to form the unwanted silacyclopentane-3-ol-4-ester, which can be further hydrolysed to give a silacyclopentane-3,4-diol.

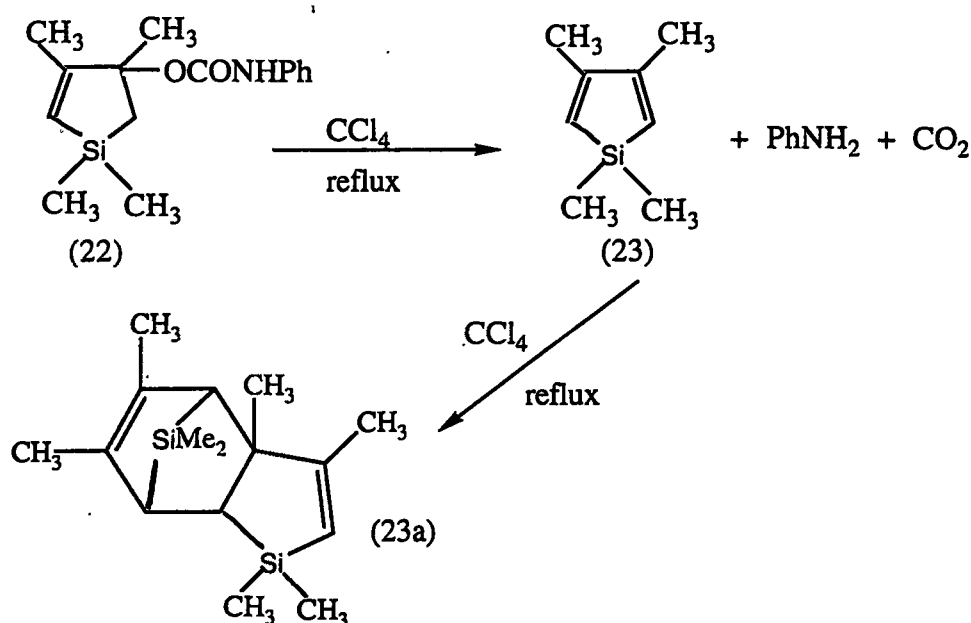


In the preparation of the allylic alcohol (21), it was found that the use of an excess of diethylamine is crucial to ensure the complete transformation of *n*-butyllithium into lithium diethylamide. If not, the butyllithium may react with the epoxide to form linear products, by cleavage of the C-Si bond, and /or remove a proton from the methyl group in position 4, to give an isomer of the alcohol, as shown below. This has been confirmed by NMR. It was also found that slow addition of the epoxide to the reaction system leads to low yields of the required product.



The preparation of 1,1,3,4-tetramethyl-1-sila-2-cyclopentene-4-N-phenylcarbamate (22) requires the use of a catalyst, dibutyltin dilaurate. This is essential to accelerate the complete transformation of the alcohol to the carbamate. Without the catalyst the transformation took a much longer

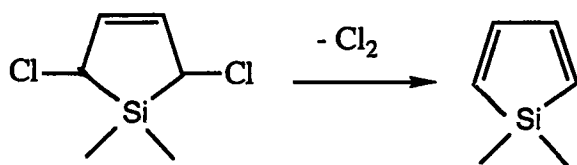
time and was incomplete. The final silole (23) was obtained by thermolysis of the carbamate (22), however, it was noted that the silole product (23) is not particularly stable and if the thermolysis was left for longer the product reacted with itself in a Diels-Alder reaction, as shown below.



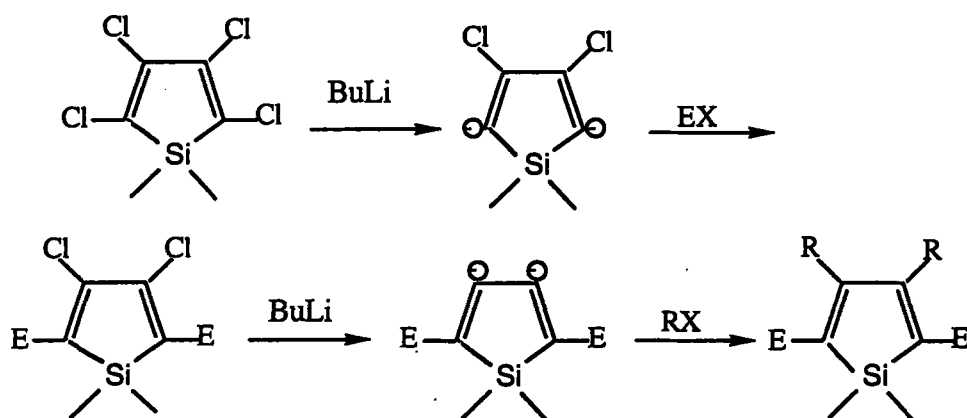
The structure and purity of these compounds (19), (20), (21), (22) and (23) were verified by FTIR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and Mass spectra as listed in the experimental section.

### 2.2.2 Attempts to prepare functionalised silole derivatives

The synthesis of silole compounds has only been achieved via multi-step routes and thus does not provide a simple procedure for the synthesis of a range of such compounds. Whilst the synthesis of the silacyclopentene seemed relatively straightforward, it is the conversion to the diene that causes the problem. One solution is to prepare the 2,5-dichlorosilacyclopentene which on elimination of chlorine gives the diene directly.



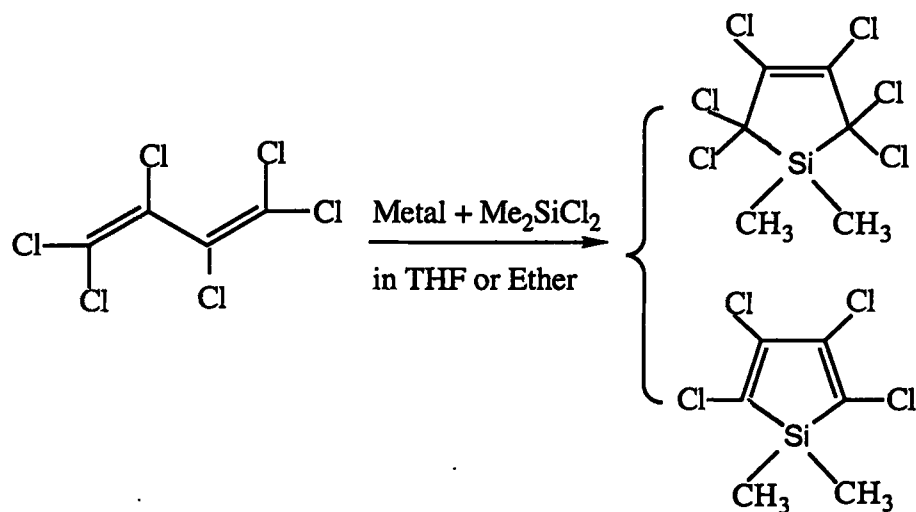
Furthermore, if the 2,3,4,5-tetrachlorosila-cyclopentadiene could be prepared, reaction with 2 equivalents of magnesium or butyl lithium would give the 2,5-dianion which could then be further functionalised. The reaction is selective for the formation of the 2,5-dianion because of the formation of  $\alpha$ -silylcarbanions. Such behaviour has also been observed with 2,5-dibromothiophene<sup>23</sup>. Reaction of the resulting compound with a further two moles of butyl lithium would then lead to functionalisation of the 3 and 4 positions. The reaction scheme is outlined below.



Alternatively, the presence of chloro groups in the 2 and 5 positions would enable the polymerisation by Grignard coupling in the presence of a Ni complex catalyst.

We hoped to prepare such a compound by the cyclisation of the commercially available hexachlorobutadiene with dichlorodimethylsilane.

### 2.2.2.1 Cyclisation of hexachlorobutadiene (HCB) with dichlorodimethylsilane



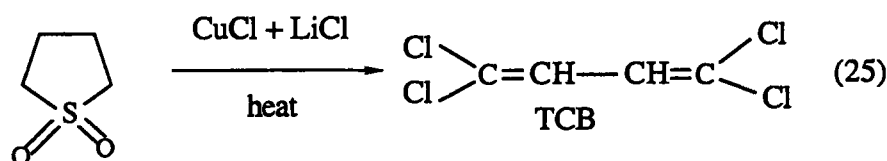
Hexachlorobutadiene was reacted with dichlorodimethylsilane in the presence of a range of active metals or alkylmetal (two equivalent), such as lithium, sodium, magnesium and butyl lithium in dry diethyl ether or THF. Unfortunately, the desired products could not be isolated. Nevertheless, the starting material, HCB, was consumed during this process. FT-IR of the products showed two strong absorption bands at  $2150$  and  $2270\text{ cm}^{-1}$  indicating the presence of carbon-carbon triple bonds in the product. These products were more favoured in THF than in ether. In ether, the HCB was consumed more slowly. Furthermore, when magnesium and THF were used a grey powder was formed which could not be dissolved in either organic or aqueous mediums. It was supposed that the HCB may have polymerised on its own or with the dichlorosilane. Repeating the reaction without the addition of the dichlorosilane gave a large amount of black powder. The IR spectrum of the black powder showed an absorption band at about  $2100\text{ cm}^{-1}$ . When other metals or butyllithium were used the black powder was hardly ever found. Nevertheless, a product containing carbon-carbon triple bonds was formed in all cases.

It was thought that the HCB was undergoing a  $\beta$ -elimination, a dehalogenation, to give 1,4-dichlorobuta-1,3-diyne or other products containing triple bonds, rather than forming the short-lived dianion. Thus, it was decided to change the target compound to 1,1,4,4-tetrachlorobutadiene (TCB) which could not undergo a 1,2-dehalogenation but which would still enable us to synthesis a range of derivatives of silole.

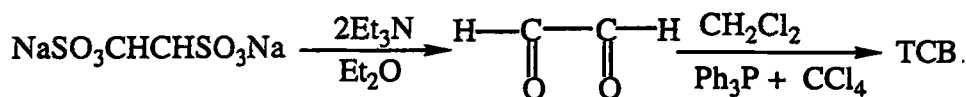
#### 2.2.2.2 Cyclisation of 1,1,4,4-tetrachlorobutadiene (TCB) with dichlorodimethylsilane

##### 1) Route to prepare tetrachlorobutadiene

At first a published route<sup>24</sup> was followed to generate TCB (25), through the reaction of sulfolane with cupric chloride and lithium chloride at 215°C. However, too many by-products were obtained which proved difficult to separate.

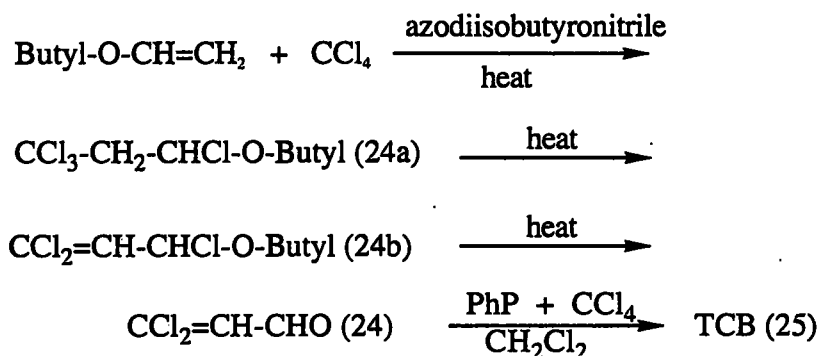


A second procedure utilised a Wittig methodology. Dichloromethylene phosphorane can be readily generated from triphenyl phosphine and carbon tetrachloride. However, glyoxal could not be readily formed from its bisulphite salt in non aqueous media, since the salt would not dissolve in any organic solvent.



Finally, an alternative route was developed to prepare TCB through the reaction of 3,3-dichloropropenal with dichloromethylene phosphorane. 3,3-dichloropropenal (24) can be made by a published method<sup>25</sup> in which n-

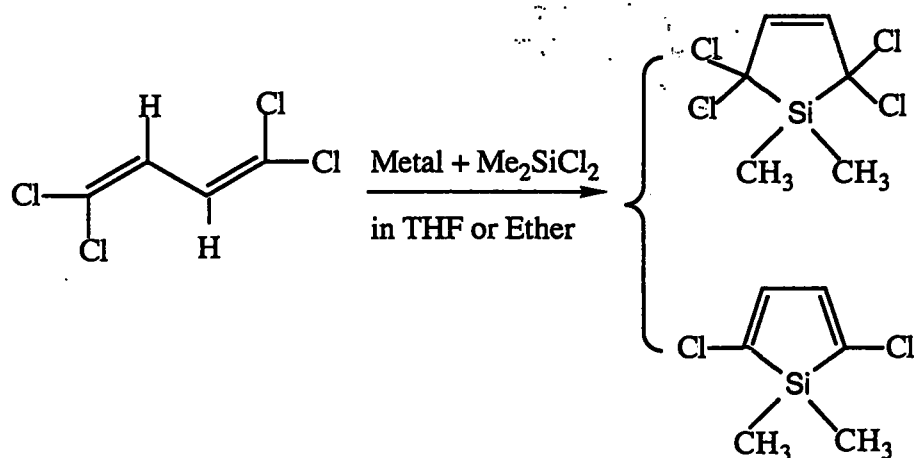
butoxyvinylether was reacted with carbon tetrachloride in the presence of azodiisobutyronitrile to give compound 24b. This was followed by pyrolysis at 150°C to obtain the dichloropropenal as shown in scheme 2-9. During subsequent reaction of 3,3-dichloropropenal with the Wittig reagent, a by-product 1,1,3,3-tetrachloropropene predominated if the dichloropropenal was added slowly to the system.



Scheme 2-9 Preparation of 1,1,4,4-tetrachlorobutadiene(TCB)

The structure and purity of the compounds (25) and (25a) were confirmed by FT-IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR and Mass spectra as listed in the experimental section.

## 2) Reaction of TCB with dichlorodimethylsilane

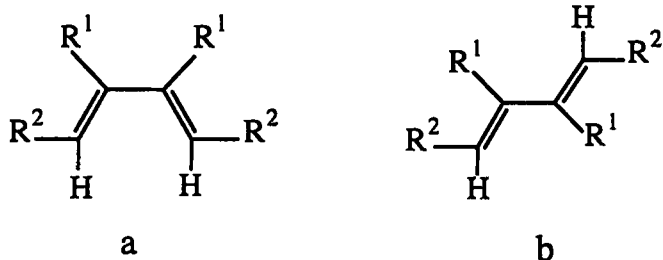


TCB was cyclised with the dichlorosilane using the same conditions as those used for HCB. Disappointingly, the NMR and mass spectra of the products

showed no signs of the silacyclopentadiene or silacyclopentene. In most cases only the starting material, TCB, was found to be present after the reaction. Studies in the absence of dichlorodimethylsilane indicated that TCB did not react readily with the metal. By monitoring the progress of the reaction using glc and glc-Mass spectrometry, it was found that the intensity of the TCB peak did not change, even after 24 hours. When n-butyllithium was used in place of the metals, TCB did indeed react. The  $^1\text{H}$  proton NMR peak at 6.6 ppm arising from TCB disappeared. Some products containing a carbon-carbon triple bond were formed, which was confirmed using FT-IR spectrometry. This indicated that the TCB may react with n-butyllithium to eliminate hydrogen chloride.

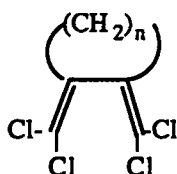
The latter result indicates that TCB may react with more active metals. It was found that TCB did react with Magnesium in the presence of ultrasound to give a range of unidentified products, with complex NMR spectra. Many peaks were present between 4 ppm and 7.5 ppm. However, no peaks corresponding to the desired cyclic silicon compounds could be seen in either NMR or Mass spectra. Thus, it was supposed that the elimination process dominated the reaction and the formation of the stable anion was unlikely.

To understand why these butadienes do not react, it is necessary to consider which types of butadiene have been reported to cyclise with dichlorosilanes to give silacyclopentadienes. Only butadiene itself and 2,3-dimethylbutadiene have been successfully cyclised. As well as TCB and HCB, hexa-2,4-diene and 1,4-diphenylbutadiene have been shown not to react with dichlorosilanes<sup>26</sup>. We suggest that in order to cyclise, the butadiene must be able to readily adopt the "*cis*" conformation (a)



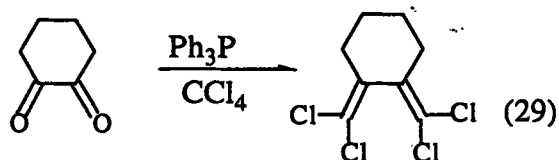
With 2,3-dimethylbutadiene the energy difference between the two conformations ( $R^2=H$ ,  $R^1=CH_3$ ) is not that large. However, if  $R^2$  is large, for example when  $R^2$  is methyl, phenyl or chloro, then the "*trans*" conformation (b) is formed and cyclisation is not possible.

To test this hypothesis we prepared an alternative tetrachloro-butadiene which cannot undergo an elimination reaction and which is locked in a "*cis*" conformation.



### 2.2.2.3 Synthesis of rigid cisoid tetrachlorobutadienes

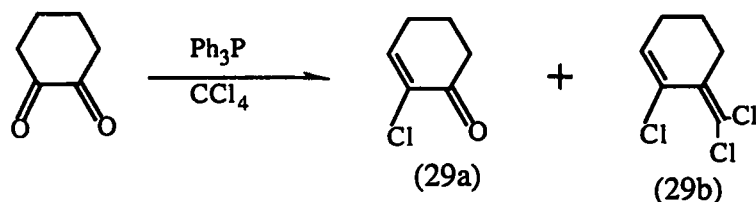
#### 1) Attempt to prepare $\alpha,\alpha,\alpha',\alpha'$ -tetrachloromethylenecyclohexane (29)



The first attempt was based on the Wittig reaction between a ketone and excess triphenylphosphine and carbon tetrachloride in THF at room temperature, or reflux, to give the corresponding dichloromethylene compound. In this work 1,2-cyclohexanedione was chosen as the starting material to be converted to  $\alpha,\alpha,\alpha',\alpha'$ -tetrachloromethylenecyclohexane (29) by reaction with 8 equivalents of triphenylphosphine and 3 equivalents of



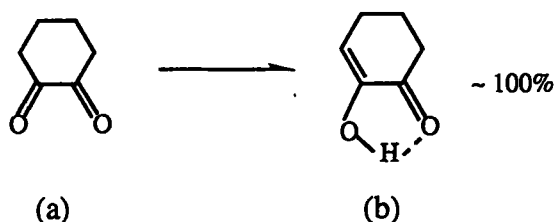
carbon tetrachloride. However, irrespective of the quantities, the final reaction mixture consisted of the mono-chloro cyclohexenone (29a) and 1-dichloromethylene-2-chloro-3-cyclohexene (29b) plus unreacted cyclohexanedione.



On raising the reaction temperature to reflux, the outcome was even more dissappointing, and the resulting products could not be identified, except for a trace of the mono-chloro olefin. Thus, two alternative methods<sup>27,28</sup> were examined.

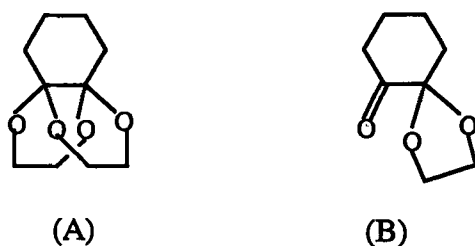
Hosomi has reported that when dichloromethyltrimethylsilane is reacted with n-butyllithium in THF at below  $-100^\circ\text{C}$  for 1 hour (trimethylsilyl)dichloromethyl-lithium is obtained. The resulting intermediate reacts directly with an aldehyde to afford the corresponding  $\beta$ -hydroxysilane. Careful hydrolysis with aqueous ammonium chloride-methanol (1:9) at below  $-80^\circ\text{C}$  leads to the dichloromethylene compound. However, when the method was used to prepare the tetrachloromethylene compound (29) from cyclohexanedione, only the mono-chloro olefin (29b) was obtained. The second method involves reaction of diethyl methylphosphonate with n-butyllithium and benzenesulfonyl chloride in THF at  $-78^\circ\text{C}$  to give the intermediate, (diethylphosphoryl)dichloromethyl lithium. Reaction of this with carbonyl compounds affords the corresponding dichloromethylene product. Again when this method was used to prepare the tetrachloromethylene compound (29), the desired product was not isolated.

It seemed that direct transformation of the 1,2-cyclohexanedione to the tetrachloromethylene compound was not possible. This is probably because of keto enol tautomerisation of the starting material as shown below.



The enol form predominates in the system (almost 100%) since the carbonyl groups are locked in the syn-conformation in both keto (a) and enol (b) forms, and the intramolecular hydrogen-bonding is open only to the enol form, but not to the keto form<sup>29</sup>. The presence of the enol form explains the predominance of compound 29b, also acidic OH proton will quench any organolithium reagent.

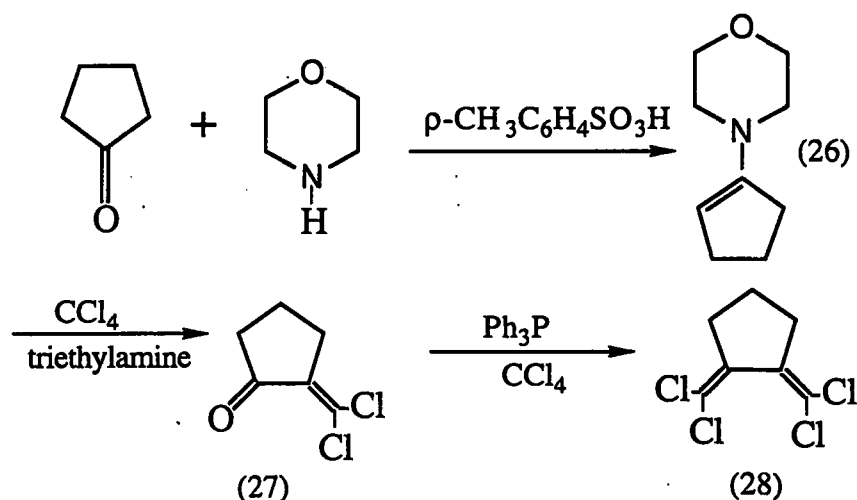
To avoid the preferential formation of the enol form a protecting group was introduced into one of the carbonyl groups which could be removed after carrying out the first Wittig reaction. A subsequent Wittig reaction would then give the desired product. One equivalent of ethylene glycol was reacted with the hexanedione in the presence of toluene-4-sulfonic acid monohydrate. A mixture consisting of diethylene ketal (A) and monoethylene ketal (B) was obtained plus the unreacted dione.



By distillation under reduced pressure the mixture could be separated. However, it was found that the diethylene ketal predominated and the yield of the desired monoethylene ketal was below 5%.

## 2) A alternative route to prepare the tetrachloromethylene compound

Since the previous route was unsatisfactory an alternative pathway to the tetrachloromethylene compound was developed. This involved the formation of the dichloromethylene derivative (27), followed by a standard Wittig reaction as outlined in Scheme 2-10.



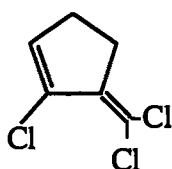
Scheme 2-10 Preparation of  $\alpha,\alpha,\alpha',\alpha'$ -tetrachloromethylene cyclopentane(28).

1-Morpholino-1-cyclopentene (26) was synthesised by the reaction of the cyclopentanone with morpholine in the presence of p-toluenesulfonic acid in toluene. The preparation of the  $\alpha$ -dichloromethylene ketone (27) was accomplished by a modification of the method of Wolinsky<sup>30</sup>. Treatment of the enamine (26) with a large excess of carbon tetrachloride at 60-70°C for 24 hours in total darkness under a nitrogen atmosphere, in the presence of 2 equivalents of triethylamine ( the triethyleamine is used as a scavenger for hydrogen chloride) gave the  $\alpha$ -dichloromethylene ketone (27) in 65% yield.

$\alpha,\alpha,\alpha',\alpha'$ -Tetrachloromethylene cyclopentane (28) was synthesised by a standard Wittig method. One equivalent of the resulting ketone (27) was stirred with four equivalents of triphenylphosphine in anhydrous acetonitrile

under nitrogen at 0°C for 30 min. The tetrachloromethylene product (28) was isolated but the yield was very low (5%), the rest being the unreacted starting ketone.

In order to improve the yield of the tetrachloromethylene compound (28) a range of conditions were employed. Bromotrichloromethane was used to replace carbon tetrachloride; 8 equivalents of triphenylphosphine were employed; increased reaction temperatures and times were tried; and the reaction was kept at -10°C for a longer time. All the results proved disappointing. The yield of the desired product was not improved and side reactions began to dominate to give the mono-chloro olefin (28b).



In all cases a large amount of the unreacted starting material remained. It seems that steric factors may prevent the conjugated  $\alpha$ -dichloromethylene ketone from reacting with the dichloromethylene phosphorane and /or the ketone tautomerised to the enol form which underwent side-reactions when the reaction was carried out at higher temperatures.

The structure and purity of these compounds were verified by FT-IR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and Mass spectra as listed in the experimental section.

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# Chapter Three

## Polymerisation and Oxidative Doping of Isothianaphthene Derivatives: Electrochemical and Pure Chemical Oxidation

### 3.1 Introduction

As discussed in chapter one the synthesis of conjugated polymers can be divided into two methods; electrochemical and conventional pure chemical polymerisations. In this study only two routes of dehydrogenative coupling of aromatic nuclei were employed to generate electroactive/conductive polymers; electrooxidation (anodic electrolysis) and oxidative coupling with Lewis acids and other chemicals. These routes have the advantage that they lead to the formation of oxidised (doped) conducting polymers (or films). The pure chemical coupling with Lewis acids is the most simple route. This was originally reported by Kovacic in 1962<sup>1</sup> for the conversion of benzene to poly(p-phenylene) by treatment with aluminum chloride/cupric chloride at mild temperatures. Most recently, this oxidation method has been extended to the preparation of polypyrrole<sup>2</sup>, polythiophene<sup>3</sup> and their derivatives<sup>4,5</sup>. Most of the final products are intractable, insoluble and have structure defects. The electrochemical process for making electroactive/conductive polymers (or films) is very versatile and provides a facile way to vary the properties of the products. Of course, this reaction is very different from electrochemically initiated reactions, where the polymerisation occurs away from the electrode, and with organic electrosynthesis where the electrode is often filmed with insulating by-product which passivates the electrode<sup>6</sup>. In contrast, this electrooxidation has a fixed electrochemical stoichiometry and the complete polymerisation

process occurs at the electrode to give polymers with electroactivity and conductivity.

Diaz and coworkers<sup>7</sup> were the first to systematically use this route to prepare highly conductive polypyrrole films. Since then, many conductive polymers have been successfully made by this general method including products from pyrrole, thiophene, azulene, pyrene, carbazole, indole, furan, aniline and their derivatives, and even some compounds which need a high potential for oxidation such as benzene and acetylene. However, the electrooxidation process is rather complicated and the reaction mechanism is still under debate. Diaz has suggested that the polymerisation involves radical cations of the monomers and this has been widely accepted. However, the successive processes are not clear. The polymerisation pathway for the thiophene family seems to involve<sup>8,9</sup>:

- a) oxidation of the monomer to a radical cation;
- b) dimerisation of the radical cations;
- c) proton loss to give a neutral dimer;
- d) oxidation of dimer to its radical cation;
- e) reaction of dimer radical cation with other radical cations and so on, leading to an oxidised conducting polymer.

The properties of the final products are strictly dependent on the electrochemical reaction conditions.

On the other hand, modification of the aromatic nucleus can drastically affect the physical and electronic properties of the resulting polymers<sup>10</sup>. In this work a range of isothianaphthene derivatives have been prepared including DHITN, ITN, DHDMITN, DMITN, MeODHITN, MeOITN, PhITNCOOH and PhITN. One of our main aims was to investigate whether the introduction of methyl, methoxy and benzene substituents into the



isothianaphthene system affected the intrinsic properties of the resulting isothianaphthene polymers. We started by systematically examining how the electrochemical cell conditions affected the polymerisation of these monomers. We chose to vary the solvents, the electrolyte salts, the electrodes and the electrochemical parameters.

Electropolymerisation of these monomers was carried out in a two-compartment cell under the protection of nitrogen with magnetic stirring at room temperature. The reaction solution was degassed by bubbling nitrogen through the solution for 10 minutes before carrying out the reaction. In most cases a platinum plate was used as the working electrode, ITO electrodes were occasionally used and these will be specifically mentioned. To compare the conductivity of the resulting polymers, powder samples were collected from the cell and the surface of the working electrode. They were extracted with acetonitrile and dichloromethane for 24 hours under nitrogen and dried in vacuo. Their conductivity was then measured by a standard method four-point probe technique. The error of reproducibility of the conductivity measurement is below  $\pm 20\%$ .

## **3.2 Electrochemical Polymerisation of Isothianaphthene and Dimethylisothianaphthene**

### **3.2.1 Effect of solvent**

A wide variety of aprotic solvents can be used in the electrochemical oxidation process, providing the nucleophilic character of the solvent is low, since the reaction has been shown to be sensitive to the nucleophiles<sup>8,9</sup>. Three solvents were used in this study, acetonitrile(MeCN), propylene carbonate(PC) and dichloromethane. The effect of solvents on the conductivity of the resulting polymers made from DHITN, DHDMITN, ITN and DMITN were investigated. Figure 3-1 shows that dichloromethane had a

dramatic effect on electrochemical polymerisation of the 1,3-dihydro compounds (DHITN and DMDHITN) in the presence of TBNBr. Only a very small amount of the product was produced even when the reaction was left for more than 24 hours. Not enough product was obtained even for a conductivity test. Most of the monomer was still unreacted.

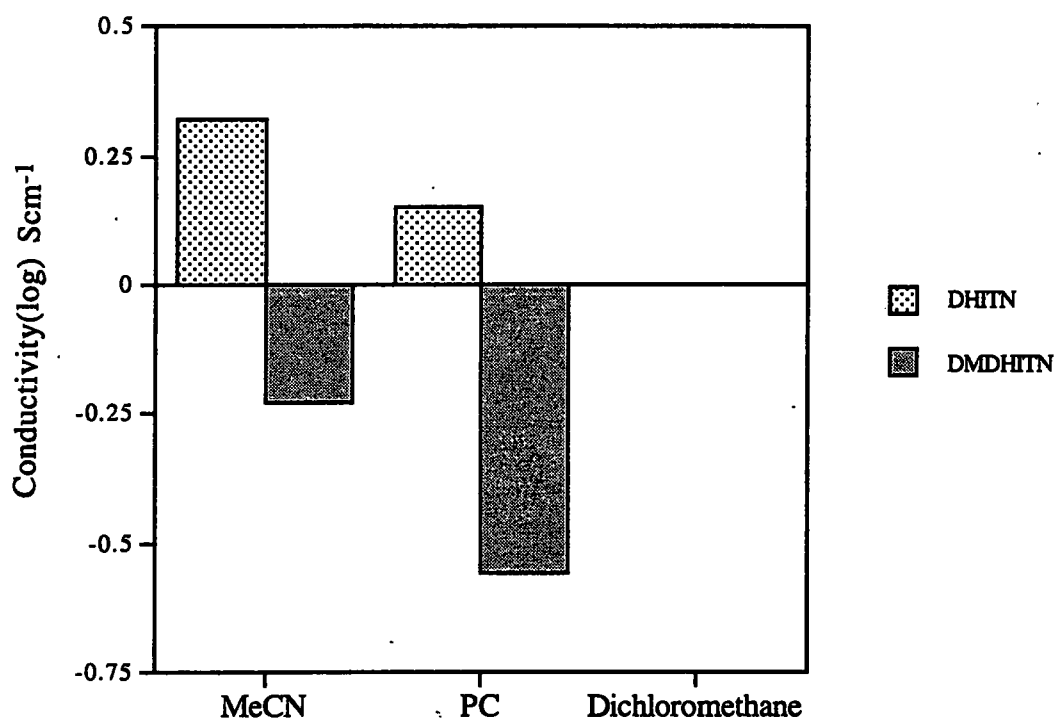


Figure 3-1 Effect of solvent on polymer conductivity for the electrooxidation of DHITN(0.2M) and DMDHITN(0.2M) respectively with a Pt electrode at 2.0v, and using TBNBr(0.2M).

In contrast, when acetonitrile and propylene carbonate were used as solvents good yields (>45%) of the final product were obtained. Both of the polymers formed from DHITN and DMDHITN had a high conductivity, comparable to that of the parent ITN reported by Wudl<sup>11</sup>. The conductivity of the product made in acetonitrile was slightly higher than that in propylene carbonate. It was also found that the polymer made from DMDHITN had a slightly lower conductivity than that of DHITN.

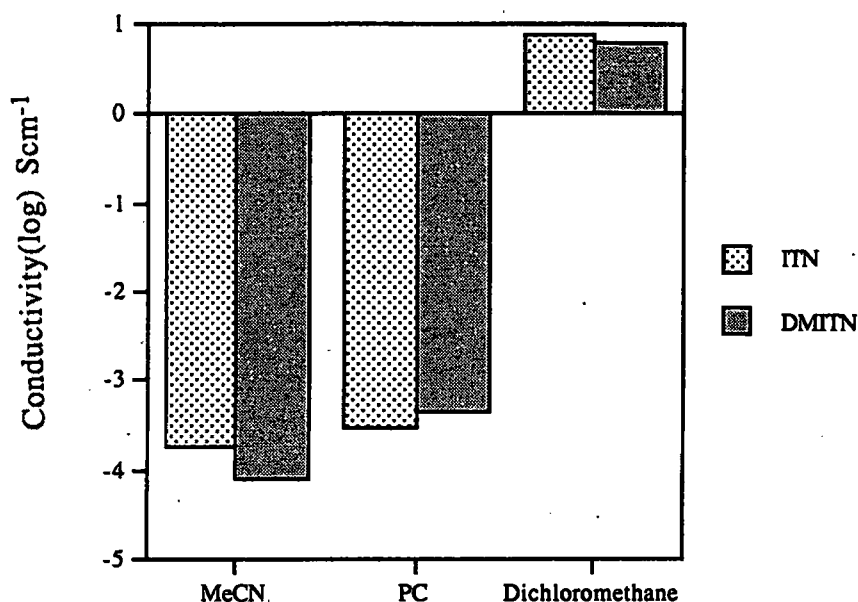


Figure 3-2 Effect of solvent on the conductivity of PITN and PDMITN formed by electropolymerisation with a Pt electrode at 2.0v, TBNBr (0.2M) as a supporting electrolyte and the monomer concentration was at 0.2M.

Figure 3-2 shows that the fully aromatic monomers( ITN and DMITN) behaved differently to the 1,3-dihydro monomers. When acetonitrile and propylene carbonate were used as the solvents the polymer formed from both ITN and DMITN has a very poor conductivity. With these solvents, a white powder was rapidly deposited on the working electrode and a precipitate formed in the solution at the beginning of electrochemical reaction. This behaviour occurred even before the reaction was carried out. Once, accidentally, the monomer was mixed with the supporting electrolyte without solvent. The resulting mixture did not dissolve in any of the three organic solvents used in this work (even in an ultrasonic bath). There seems to be an 'association' between the monomer and the electrolyte such that precipitation takes place on addition of the supporting electrolyte.

When the monomer and electrolyte solutions were made up separately using dichloromethane as the solvent, then mixed together, no white powder was seen. Figure 3-2 shows that using dichloromethane as the solvent

significantly improves the conductivity of the polymer formed from both ITN and DMITN. It seems that the use of dichloromethane may avoid the 'association' between the aromatic monomer and the electrolyte. Figures 3-1 and 3-2 indicate that when choosing a solvent we should not only consider the nucleophilic behaviour but also the solubility.

The formation of a white powder was also reported by Wudl<sup>11</sup> during electropolymerisation of ITN . It was mentioned that the white powder may be polydihydroisothianaphthene (examined by Infrared spectroscopy). However, The white powder was not found in the polymerisation of the 1,3-dihydro monomers even though they probably lead to the same polymer as ITN and DMITN. The details of these electrochemical reactions will be presented in the following chapter.

### **3.2.2 Effect of electrolyte**

Although the conductivity of the polymers is generally dependent on the potential used for the electropolymerisation<sup>9</sup>, the nature of the electrolyte anions can also influence the conductivity to some extent<sup>12,13</sup>. Generally, the choice of the supporting electrolyte depends on factors such as the solubility, degree of dissociation and nucleophilicity. In this study owing to the selection of three aprotic solvents, tetraalkylammonium salts were mainly used. Only one lithium salt was used for comparison, because the metal salts were highly aggregated and not very soluble in aprotic solvents. The electrolytes investigated in this work included tetrabutylammonium bromide (TBNBr), tetraethylammonium tetrafluoroborate (TENBF), Tetraethylammonium p-toluenesulphonate (TENTS), lithium perchlorate (LiClO<sub>4</sub>), tetrabutylammonium iodide (TBNI) and tetrabutylammonium hydrogen sulfate (TBNHS).

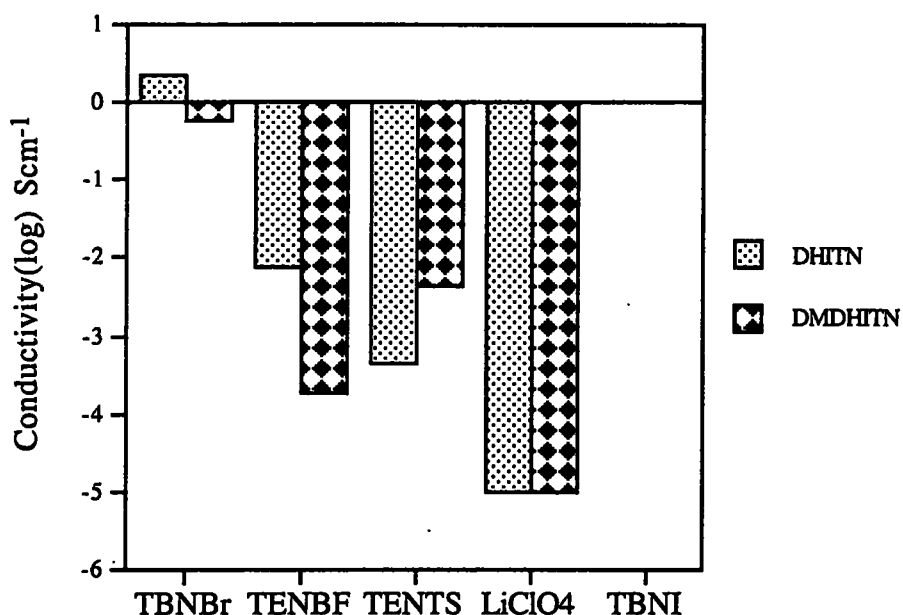


Figure 3-3 Effect of supporting electrolyte on the conductivity of the polymer formed by the electrooxidation of DHITN(0.2M) and DMDHITN(0.2M) respectively using a Pt electrode at 2.0v in acetonitrile. The supporting electrolyte concentration is 0.2M.

It is clear from Figure 3-3 that of these electrolytes, TBNBr, a nucleophilic electrolyte, was the most effective supporting electrolyte. However, when TBNI was used, neither monomer could be converted to a polymer. After work up, no deposit was found and most of the monomer still remained in solution, even though the solution was deeply coloured. It was thought that the electrolyte had undergone an oxidation reaction, at the polymerisation potential, to give a free iodine(I<sub>2</sub>) which coloured the solution. Even at a low potential (1.2v) the electrolyte reacted and no deposit was formed.

When LiClO<sub>4</sub> was used the conductivity of the resulting polymers was lower than 10<sup>-5</sup> Scm<sup>-1</sup> and the polymer was deep brown rather than black. Nevertheless, a high yield of polymer (60%) could be obtained. Based on the conductivity of the polymers, TENBF and TENTS were better electrolytes than LiClO<sub>4</sub> but worse than TBNBr. Interestingly, TENBF was slightly

better for the polymerisation of DHITN and TENTS was slightly better for the polymerisation of DHDMITN.

When TBNHS was used as an electrolyte a thin brown, very adhesive film was deposited on the Platinum working electrode at the beginning of the reaction. When the thin film had totally covered the active surface of the working electrode the electropolymerisation ceased and none of the monomer was further consumed. Thus, this indicates that the resulting thin film was not the desired product but an insulator.

These electrolytes were also used in the electrooxidation of the fully aromatic compounds (ITN and DMITN) in dichloromethane. The results were similar to those of the 1,3-dihydro compounds. In both cases, when the nucleophilic electrolyte, TBNBr, was used, not only was the highest conductivity achieved, but also the quality of electro-optical active films was the highest. This behaviour is to some extent unusual. Diaz and Bargon<sup>8</sup> suggested that when the anion of the electrolyte is a halide, good films are not usually obtained, because halides are fairly nucleophilic and easily oxidized. However, in our studies only TBNI seemed to agree with this suggestion. When other non-nucleophilic electrolytes were used, the films deposited on the working electrode were very fragile and a black powder with poor conductivity predominated in the system.

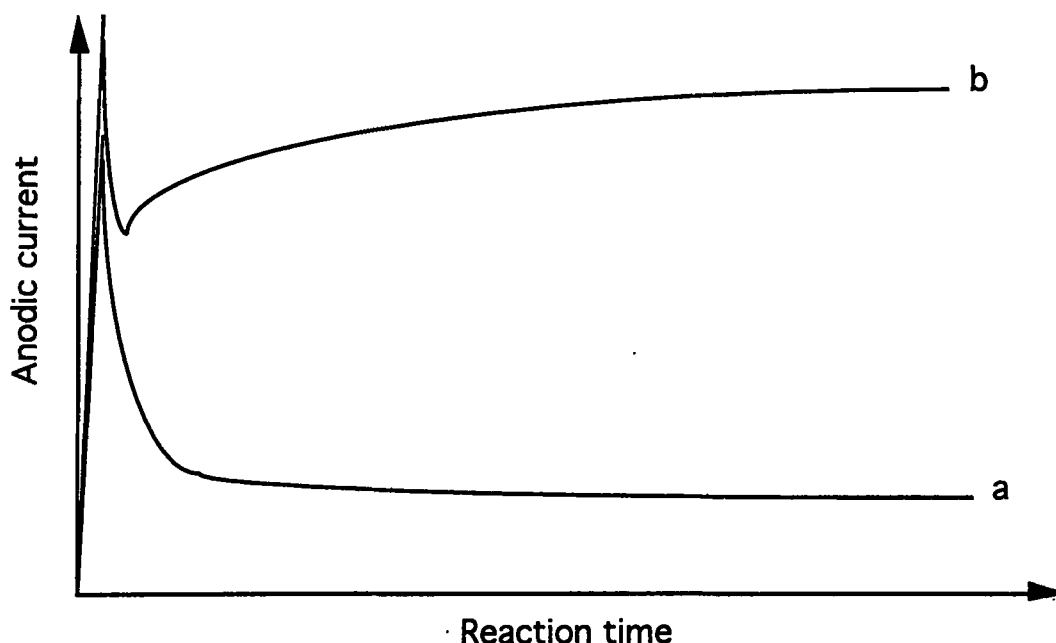


Figure 3-4 Current change during electropolymerisation of DHITN(0.1M) on a Pt electrode at the constant potential of 2.0v vs. Ag/AgCl. a): Using TENBF(0.2M), b): Using TBNBr(0.2M).

Examination of the change in current during electropolymerisation showed that when the non-nucleophilic electrolyte (TENBF) was used, the reaction current rose then decreased sharply, while an anodic constant potential was applied as shown in Figure 3-4(Curve a). In contrast, when the nucleophilic electrolyte (TBNBr) was used, the reaction current steadily increased until it reached a limiting value as shown in Figure 3-4(Curve b). This indicates that when a highly electroactive product is deposited on the working electrode the active surface of the electrode increases. However, when a poorly conducting powder or oligomer is formed on the electrode the active surface of the electrode decreases. the former leads to enlargement of the current passing through and the latter diminishes the reaction current.

### 3.2.3 Effect of electrode

Two types of working electrodes were examined, platinum plate (Pt) and transparent indium-tin oxide (ITO) coated glass. They have both been extensively utilised in the electropolymerisation of thiophene and its

derivatives. Platinum is very inert to most chemical environments, and the ITO electrode is transparent so that the electroactive film formed on its surface can be investigated spectroscopically. Generally speaking, the polymers of ITN and its derivatives deposited on the ITO electrode exhibited a higher conductivity than the polymers deposited on the platinum electrode, as shown in Figures 3-5 and 3-6. By using the ITO electrode highly conducting polymers were obtained from the 1,3-dihydro compounds, DHITN and DHDMITN, even when the non-nucleophilic electrolyte(TENBF) was used as a supporting electrolyte. When the platinum was used as the electrode in the presence of TENBF the conductivities were quite disappointing.

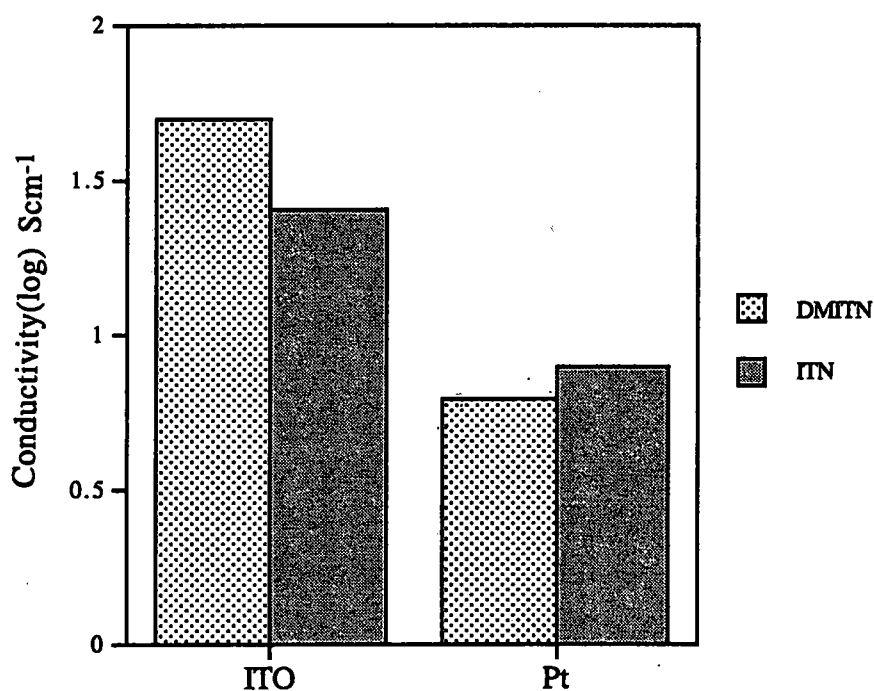


Figure 3-5 Effect of working electrode on the conductivity of the polymer formed by the electropolymerisation of ITN(0.2M) and DMITN(0.2M) respectively in dichloromethane at 2.0v in the presence of TBNBr(0.2M).



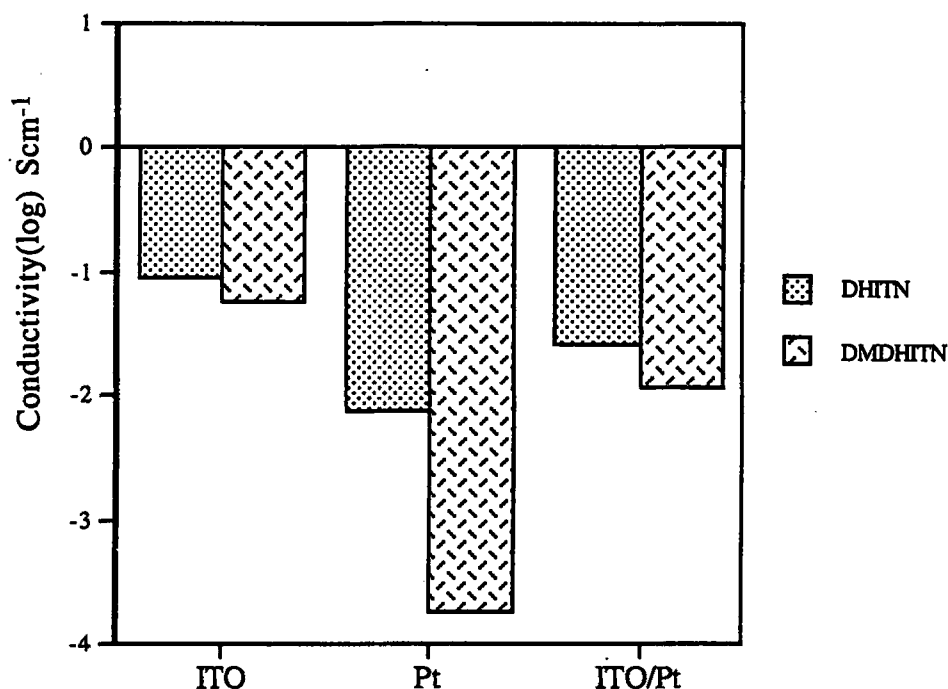


Figure 3-6 Effect of working electrode on the conductivity of the polymer formed by the electrooxidation of DHITN(0.2M) and DMDHITN(0.2M) respectively in acetonitrile at 2.0V when TENBF (0.2M) was used as a supporting electrolyte.

Unfortunately, when ITO was used as the electrode, a low yield of the product (~5%) was obtained, compared to the platinum electrode (~50%). In order to improve the yield of the product, the electropolymerisation was carried out for 10 hours using an ITO electrode. The deposit was then filtered off under nitrogen. The ITO was replaced with a platinum electrode and the reaction re-started. On re-starting the reaction, a large amount of powder was deposited on the Platinum plate. Surprisingly, this procedure not only improved the yield, but also improved the conductivity of the polymers, compared to those formed directly using a platinum electrode. The obvious difference between using these two electrodes was the reaction current. When carrying out the electropolymerisation at the same applied potential (2.0v) with the same electrode surface (4 cm<sup>2</sup>), the reaction current passing through the ITO electrode was much smaller than when a platinum

electrode was used. It seems that the reaction current is an important factor in controlling both the quality and quantity of the products obtained at a given polymerisation potential.

Of course, the conductivity of the polymers (or films) was also dependent on the nature of the electrode itself. By pre-treatment of the platinum plate with a mixture of concentrated hydrochloric acid and nitric acid (3:1), followed by rubbing it with active alumina, to make the surface of the platinum plate rough, high quality electro-optical active thin films could be made from ITN and DMITN ( 0.05 M monomer, 0.1M TBNBr and using dichloromethane as a solvent).

#### **3.2.4 Effect of applied potential**

Every monomer has its own oxidation potential and shows an irreversible oxidation peak in its cyclic voltammogram. During an electro-polymerisation the applied potential should be higher than the oxidation potential of the monomer to enable the formation of radical cations from the monomer. The applied potential also affects the current passing through the cell. Thus, the electrochemical potential is a key parameter for the production of highly conducting products (or a good electroactive film). The electrochemical activities of all the monomers and their polymers are extensively reviewed in the following chapters, as well as the mechanism of polymerisation of the isothianaphthene family. In this section the effect of applied reaction potential on the conductivity of polymers formed from ITN, DMITN, DHITN and DHDMITN is reported.

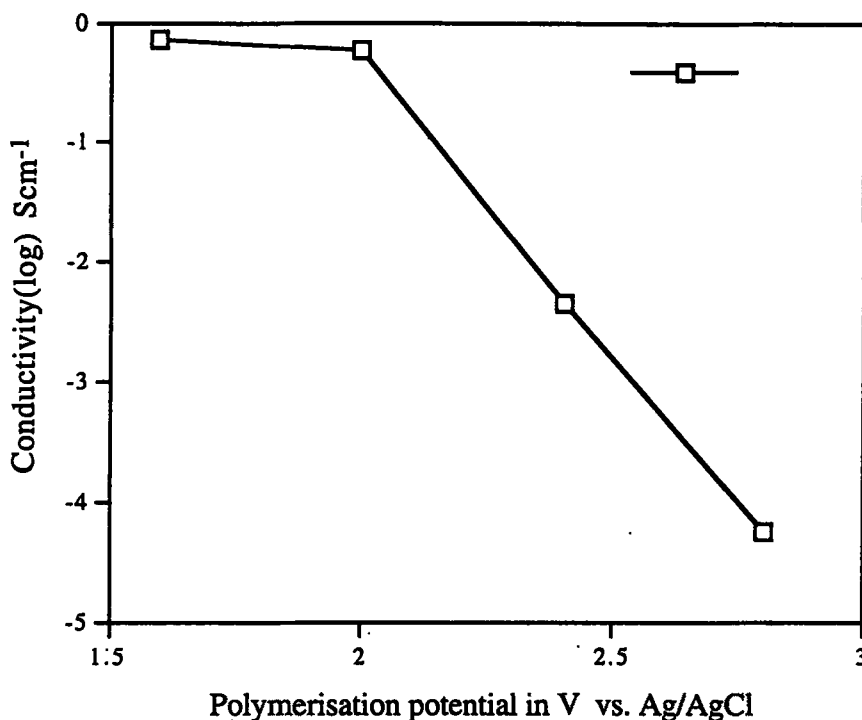


Figure 3-7 Effect of polymerisation potential on the conductivity of the polymer formed by the electrooxidation of DMDHITN with a Pt electrode in acetonitrile in the presence of TBNBr(0.2M).

Using DHDMITN as a typical example, Figure 3-7 shows that when the applied potential was lower than 2.0v the resulting polymer was highly conductive. Increasing the applied potential above 2.0v, the conductivity of the resulting polymer sharply decreased. At the higher potentials the product deposited on the working electrode was probably over-oxidised and degraded. Alternatively when a high potential was applied this led to a high reaction current which upset the balance between the formation and coupling processes of the radical cations. Thus, a large proportion of the radical cations of the oligomer could diffuse away from the electrode without undergoing further coupling and re-oxidation. This is explained in detail later when the electro-spectral studies of the monomers is described.

The polymerisation of DHITN, ITN and DMITN behaved similarly to DHDMITN. When a low potential was applied the resulting polymer was highly conducting. High reaction potentials over 2.0v, diminished the

conductivity. The yield of the product was dependent on the applied potential, however, the trend was the opposite of that of the conductivity.

### 3.2.5 Effect of concentration of electrolyte and monomer

The effect of the concentration of the supporting electrolyte, TBNBr, on the the conductivity of the resulting polymer was determined by keeping the concentration of the monomer, DHDMITN, constant while varying the concentration of TBNBr. Throughout this work it was found that when the concentration of the electrolyte was lower than that of the monomer the resulting polymer always had a low conductivity. Conversely, the polymer exhibited a higher conductivity when the concentration of TBNBr was higher than that of the monomer DHDMITN. The results are shown in Figure 3-8.

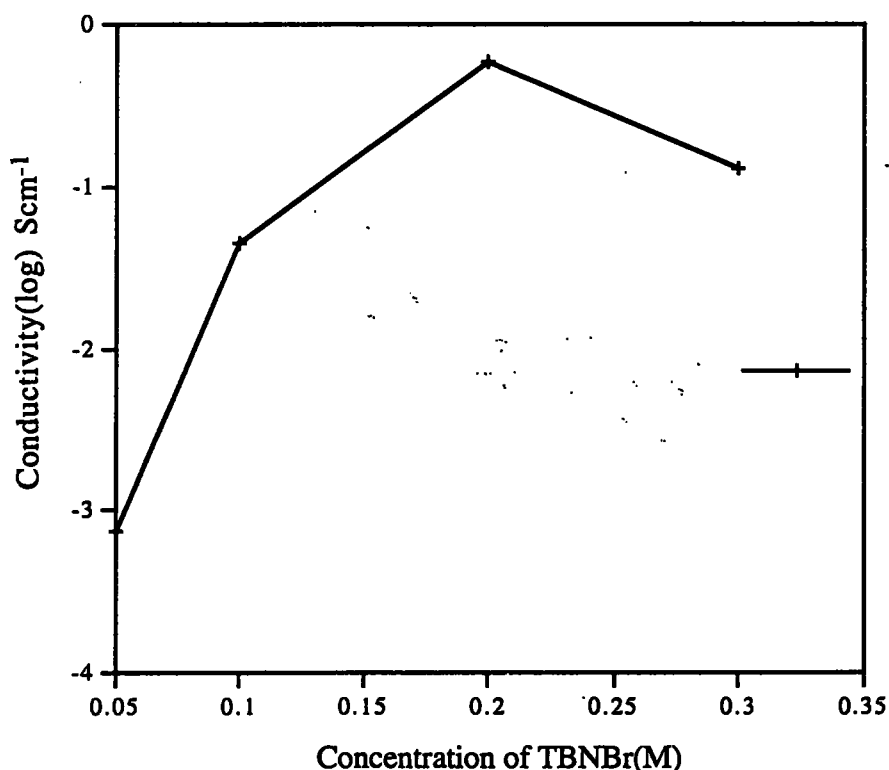


Figure 3-8 Effect of TBNBr concentration on the conductivity of the polymer formed by the electrooxidation of DMDHITN(0.2M) with a Pt electrode in acetonitrile at 2.0v.

The results suggest that a high concentration of TBNBr ensures that the resulting polymer is efficiently doped during the electrochemical oxidation. In this case, unlike the effect of reaction potentials, the high reaction current, caused by adding a high concentration of TBNBr, does not decrease the conductivity of the polymer.

The results described in Section 3.2, suggest that the introduction of methyl substituents on positions 5 and 6 of an isothianaphthene ring do not greatly affect the inherent conductivity of the parent isothianaphthene polymer. Polymers formed from both the parent isothianaphthene and its dimethyl derivative under optimum conditions had a conductivity with the same magnitude ( $10^1 \text{ Scm}^{-1}$ ). The 1,3-dihydro monomers (DHITN and DHDMITN) could be electrochemically polymerised and the conductivity of the resulting polymers was similar to that of the polymers formed from their fully aromatic derivatives (ITN and DMITN). This is consistent with the report by Gumbs<sup>14</sup> in which DHITN was readily electrochemically polymerised.

### **3.3 Oxidation of Isothianaphthene and Dimethyloisothianaphthene with Lewis Acids and Other Chemicals**

In addition to the catalytic coupling of Grignard reagents of 2,5-dibromothiophene by nickel salts<sup>15</sup> to give polythiophene in its undoped insulating state, polythiophene in its doped conducting state could be directly prepared by oxidative coupling of thiophene using a catalyst-oxidant system. Examples of such catalyst-oxidants are nitrosonium salts ( $\text{NOPF}_6$  and  $\text{NOBF}_4$ )<sup>16</sup>, ferric chloride<sup>17</sup> and pentafluoroarsenate<sup>18,19</sup>. Polymerisation by oxidative coupling initially involves the formation of radical cations from the monomer. There is an extensive review concerning the polymerisation of benzene by oxidative coupling using catalyst-oxidant systems<sup>20</sup>. However,

the mechanism of polymerisation of aromatic heterocyclic compounds using catalyst-oxidant systems has not been fully determined. Many of the reports of the preparation of polythiophene by treatment with oxidants have only been concerned with the fact that conducting polythiophene could be obtained under such conditions. For isothianaphthene and 1,3-dihydroisothianaphthene there have been reports of pure chemical polymerisation using N-chlorosuccinimide (NCS), ferric chloride, sulfuric acid, oxygen and other chemicals<sup>11,21,22,23</sup>. The conductivity of the resulting polymers are between  $10^{-2}$  and  $10^{-1}$  s/cm. In this work a comparison of the polymerisation of 5,6-dimethylisothianaphthene with the parent isothianaphthene was examined using a variety of catalyst-oxidant systems. Ferric chloride( $\text{FeCl}_3$ ), aluminum chloride( $\text{AlCl}_3$ ), cupric chloride( $\text{CuCl}_2$ ), and trifluoroacetic acid( $\text{CF}_3\text{COOH}$ ) were used as oxidants. Further doping (oxidation) of the polymers formed from the four monomers (DHITN, ITN, DHDMITN and DMITN) with iodine or chloranil was also examined.

### **3.3.1 Oxidation with $\text{FeCl}_3$ , $\text{CuCl}_2/\text{AlCl}_3$ and $\text{CF}_3\text{COOH}$**

The fully aromatic monomers (ITN and DMITN) were investigated. It was found that both monomers could easily be converted to the corresponding polymers in the presence of ferric chloride or a mixture of aluminum chloride and cupric chloride. Black powders were obtained in each case. The yield of the resulting polymer from ITN (80%) was higher than that of the polymer from DMITN (65%). The conductivity of the resulting polymers showed a similar trend. PolyITN had a higher conductivity than PolyDMITN. Of the two oxidant systems ferric chloride was better than aluminum chloride. The conductivity of the polymers was higher when ferric chloride was used than when aluminum chloride and cupric chloride were employed. When trifluoroacetic acid was used as a catalyst the conductivity and yield of the polymer was very low. The product yield was

below 40% and was deep purple in colour. The polymer could be dissolved in chlorobenzene at 100°C. The conductivity of the polymer was extremely low ( $<10^{-5}$  s/cm).

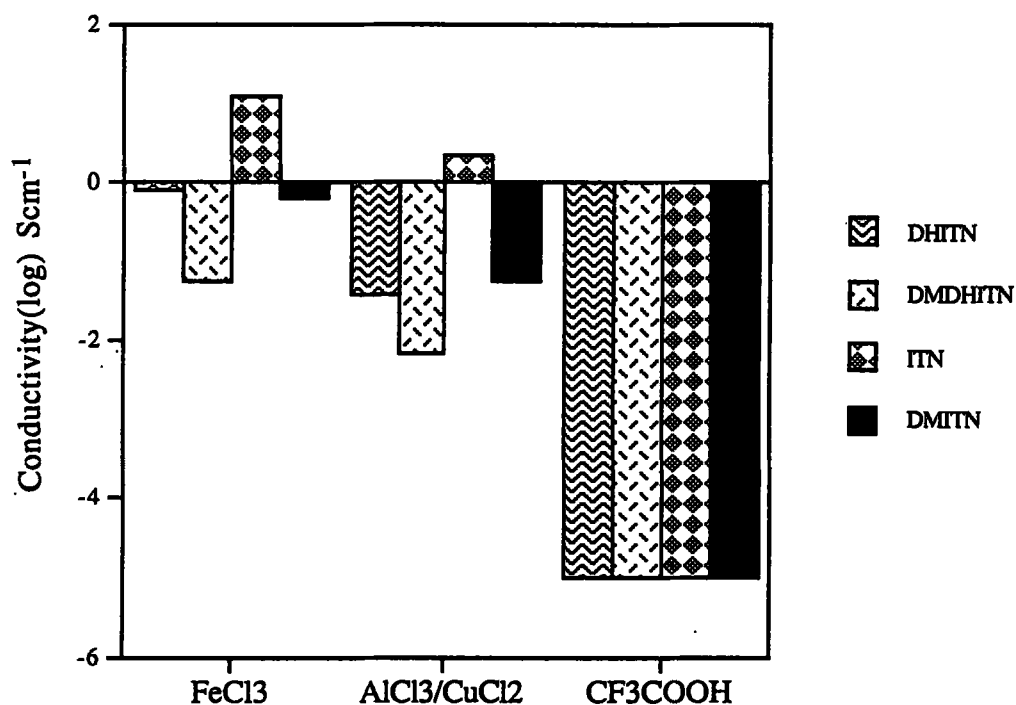


Figure 3-9 Effect of oxidising agent on the conductivity of the polymer formed by the chemical oxidation of isothianaphthenes.

Both the 1,3-dihydro monomers (DHITN and DMDHITN) could be successfully converted into conducting polymers. The effect of catalyst-oxidants on the conductivity of the resulting polymers was similar to the fully aromatic monomers. However, there were some general differences between the fully aromatic monomers and their 1,3-dihydro derivatives. With the dihydro monomers the rate of formation of polymer was lower and the resulting polymers had a lower conductivity. Even though the reaction was left for 3 days the yield of both polymers did not reach 40%. In the presence of trifluoroacetic acid the yield of the products was below 10%. It was also found that the conductivity of the polymer from DHITN

was slightly higher than that of the polymer from DHDMITN. The results are summarised in Table 3-1 and Figure 3-9.

Table 3-1 Summary of polymerisation results using catalyst-oxidant systems

| Monomer | Oxidising agent                      | Reaction time | Result*   |
|---------|--------------------------------------|---------------|---|
| ITN     | FeCl <sub>3</sub>                    | 2 days        | black powder(80%),<br>12.02 Scm <sup>-1</sup>                     |
|         | CuCl <sub>3</sub> /AlCl <sub>3</sub> | 2 days        | black powder(80%),<br>2.19 Scm <sup>-1</sup>                      |
|         | CF <sub>3</sub> COOH                 | 3 days        | deep purple deposit(<40%),<br><10 <sup>-5</sup> Scm <sup>-1</sup> |
| DMITN   | FeCl <sub>3</sub>                    | 2 days        | black powder(65%),<br>0.60 Scm <sup>-1</sup>                      |
|         | CuCl <sub>3</sub> /AlCl <sub>3</sub> | 2 days        | black powder(65%),<br>0.057 Scm <sup>-1</sup>                     |
|         | CF <sub>3</sub> COOH                 | 3 days        | deep purple deposit(<40%),<br><10 <sup>-5</sup> Scm <sup>-1</sup> |
| DHITN   | FeCl <sub>3</sub>                    | 3 days        | black powder(<40%),<br>0.76 Scm <sup>-1</sup>                     |
|         | CuCl <sub>3</sub> /AlCl <sub>3</sub> | 3 days        | black powder(<40%),<br>0.038 Scm <sup>-1</sup>                    |
|         | CF <sub>3</sub> COOH                 | 4 days        | deep purple deposit(<10%),<br><10 <sup>-5</sup> Scm <sup>-1</sup> |
| DMDHITN | FeCl <sub>3</sub>                    | 2 days        | black powder(<40%),<br>0.055 Scm <sup>-1</sup>                    |
|         | CuCl <sub>3</sub> /AlCl <sub>3</sub> | 2 days        | black powder(<40%),<br>0.007 Scm <sup>-1</sup>                    |
|         | CF <sub>3</sub> COOH                 | 3 days        | deep purple deposit(<10%),<br><10 <sup>-5</sup> Scm <sup>-1</sup> |

\*: The results record the nature, yield and conductivity of the polymers.

These results suggest that the presence of dimethyl groups do affect the oxidation process leading to polymers with lower conductivity. One proposal is that the methyl substituents stabilise the resulting radical cations.



This decreases the rate of the radical cation coupling, thus reducing the degree of polymerisation.

Furthermore, when diethyl ether was used instead of the aprotic solvents, acetonitrile or dichloromethane, no reaction took place and there was no colour change with either monomer over a long period (24 hours) even in the presence of an oxidising agent (ferric chloride or trifluoroacetic acid). Why the oxidation of the monomers should depend on the solvent is unclear. There has been no mention of such behaviour in the literature. The solvent may have an effect on the formation of the radical cations.

### **3.3.2 Further oxidation with iodine or chloranil**

Both electro and pure chemical oxidation gave some polymers which had a very low conductivity, below  $10^{-5} \text{ Scm}^{-1}$ . An explanation of why polymers with a low conductivity are sometimes formed has been put forward by Wudl<sup>11</sup>. He suggested that the resulting polymer is possibly polydihydroisothianaphthene rather than the conjugated polyisothianaphthene. A cationic chain growth polymerisation may have occurred to give an unconjugated polymer.

To test this, we examined the polymers with a low conductivity obtained from either electrochemical or pure chemical oxidation. Compared to the insoluble high conducting polymers these could be partially dissolved in chlorobenzene to give a purple colour. The polymer samples were further doped with either iodine in carbon tetrachloride or chloranil in toluene. The conductivity of all the samples improved on doping with both the oxidants. However, it was found that although the conductivity increased to about  $10^{-2}$  to  $10^{-3} \text{ Scm}^{-1}$ , they never reached the conductivity obtained via polymerisation under optimum conditions.

Two suggestions were proposed to explain this behaviour. The original products may not be long chain polymers but oligomers or short chain polymers. During the second oxidising process the radical cations of the oligomers or the short chain polymers may couple with each other to give medium-size polymers. However, the resulting medium-size polymers were not converted further to long chain polymers due to the high stability and delocalisation of their radical cations. This suggestion assumes that long conjugated chain polymers would show a higher conductivity than short chain polymers. An alternative suggestion is that the original polymer may possess defects in the polymer chain, so that the effective conjugated chain length is small and the conductivity is low. Whilst further doping with iodine leads to dehydrogenation and thus increases the effective conjugated chain length of the polymer, only some of defects are removed. The mechanism of the oxidation will be discussed further in the next two chapters.

### **3.4 Preparation and Oxidation of Poly(4-methoxyisothianaphthene)**

Polymerisation of isothianaphthene and dimethylisothianaphthene by electro and pure chemical oxidation has been discussed above. Both give polymers that have a conductivity of about  $10^1 \sim 10^2 \text{ Scm}^{-1}$  under the optimum reaction conditions. The choice of electrolytes, solvents and catalysts has been shown to have a large effect on the properties of the resulting polymers. One of the aims of this work was to find out how the methoxy substituent affects the polymerisation process and how the corresponding polymer differs from the polymer made from ITN and DMITN. In this section both electro and pure chemical oxidation of MeODHITN is discussed.

### **3.4.1 Effect of electrolyte on electrochemical polymerisation of MeODHITN**

Unlike DHITN, ITN, DHDMITN and DMITN, TBNBr could not be used as a supporting electrolyte to polymerise MeODHITN. No deposit or film was formed on the working electrode or in solution, irrespective of the reaction conditions. Changing the solvents (acetonitrile, propylene carbonate and Dichloromethane), working electrodes (Platinum plate or ITO), concentrations of the monomer and the electrolyte, and the applied potentials did not alter the outcome.

In all cases, a deep brown coloured species was seen extending into the solution from the working electrode. Glc was used to monitor the concentration of the monomer during the reaction. A sample was collected from the working cell at intervals and directly injected into the glc. From the glc trace it was confirmed that the monomer is consumed, however, no polymer was formed. We suggest that the radical cation formed from the monomer may react with Br<sup>-</sup> to give an unidentified by-product rather than couple to give the polymer. To test this the solvent was evaporated under vacuum, at the end of the reaction, to obtain a black oil-like residue. The residue was examined by NMR and Mass spectroscopy. It was confirmed that only a trace of the starting material (MeODHITN) remained but the products could not be identified.

When a non-nucleophilic electrolyte, such as TENBF or TBNPF, was used, a brown coloured deposit was formed on the working electrode {a Platinum plate, in acetonitrile, constant potential(2.0v)}. The yield of the product was up to 50%(see Table 3-2). The deposit dissolved in many organic solvents (dichloromethane, chloroform and so on) but did not dissolve in acetonitrile. This polymer was physically different to those made from the parent

isothianaphthene and its dimethyl analogue which were black and insoluble in common organic solvents.

During the electrooxidation of MeODHITN a film rapidly formed on the electrode and no pink coloured species developed, as was observed using ITN and DMITN. The resulting product had a low conductivity, below  $10^{-6} \text{ Scm}^{-1}$ . After doping with a saturated iodine solution in acetonitrile for 36 hours under argon, the conductivity of the product increased to about  $10^{-3} \sim 10^{-4} \text{ Scm}^{-1}$ . The product could also be cast as a film on a glass plate after dissolving in dichloromethane. After doping in a vacuum with iodine vapour the conductivity of the film increased to about  $10^{-3} \text{ Scm}^{-1}$ . The magnitude was similar to that of the doped powder sample. The samples doped with iodine no longer dissolved in any common organic solvent.

When an oxidant (trifluoroacetic acid or ferric chloride) was used to the chemically polymerise MeODHITN the solution in dichloromethane gradually turned pale blue. No pink colour developed during the reaction, unlike the DHITN and DHDMITN systems, and no deposit was formed. The reaction was monitored in-situ by NMR. The  $^1\text{H}$  peaks contributed by the monomer were strong and the peak positions did not shift. A large amount of the monomer remained unreacted after two days at room temperature. The only change which could be observed was the development of a blue colour in the solution.

### **3.4.2 Copolymerisation of MeODHITN and DHITN**

A mixture of the two monomers (MeODHITN and DHITN) in a 1:1 mole ratio in acetonitrile was subjected to electrochemical oxidation. Table 3-2 shows the results. Surprisingly, when TBNBr was used neither of the monomers could be converted to a polymer and no deposit was formed. After work up the residue was examined by NMR. The spectrum confirmed

that the DHITN monomer remained unreacted but only a trace of MeODHITN could be seen. We may have expected the DHITN to undergo polymerisation on its own. However, it may be that the side reaction of MeODHITN with  $\text{Br}^-$  predominated in the system so that the radical cation of the DHITN monomer could not be formed and thus the further polymerisation could not take place. Glc monitoring confirmed that the rate of consumption of the MeODHITN monomer was faster than that of DHITN.

Table 3-2 Summary of polymerisation conditions for MeODHITN

| 1) Electrochemical polymerisation |   |                                  |  |
|-----------------------------------|---|----------------------------------|--|
| Monomer(mole ratio)               |   | Reaction condition               | Result   |
| MeODHITN                          |   | TBNBr/acetonitrile at 1.4 ~ 2.4v | no deposit, the monomer was consumed   |
|                                   |   | TENBF/acetonitrile at 2.0v       | brown powder, $\sigma < 10^{-6} \text{ Scm}^{-1}$ , the yield < 50%            |
| MeODHITN/DHITN(1:1)               |   | TBNBr/acetonitrile at 1.4 ~ 2.4v | no deposit, MeODHITN was consumed and DHITN remained                           |
|                                   |   | TENBF/acetonitrile at 2.0v       | black powder, $s < 10^{-6} \text{ Scm}^{-1}$ , both the monomers were consumed |
| 2) Pure chemical oxidation        |   |                                  |  |
| Monomer                           | Oxidising agent                         | Reaction time                    | Result   |
| MeODHITN                          | FeCl <sub>3</sub> in dichloromethane    | 5 days                           | no deposit, blue solution, the monomer was only partially consumed             |
|                                   | CF <sub>3</sub> COOH in dichloromethane | 14 days                          | no deposit, blue solution, a large amount of the monomer remained              |

When TENBF was used as the electrolyte a large amount of a black deposit was formed on the working electrode or in the solution. Glc showed the rate of consumption of both monomers to be about the same. This indicates that both monomers could be electrochemically oxidised to form a copolymer or a mixture of two homopolymers. It is believed that the deposit is most likely

the copolymer, since it did not dissolve in dichloromethane, unlike the MeODHITN homopolymer. Unfortunately, the conductivity of the resulting product was not improved (below  $10^{-6} \text{ Scm}^{-1}$ ). After doping with a saturated iodine solution in carbon tetrachloride the conductivity was increased to about  $10^{-3} \text{ Scm}^{-1}$ .

### **3.5 Attempts to prepare polyphenanthrenethiophene**

Polymerisation of the more conjugated phenanthrenethiophene (PhITN) may well lead to a polymer with small band gap. Unlike the other derivatives of isothianaphthene, PhITN was very stable in air and did not change colour, even after it was stored at room temperature for six months. The results of polymerisation of PhITN are discussed below.

#### **3.5.1 Attempt to prepare a PhITN homopolymer**

Based on previous experience, several attempts were made to polymerise PhITN using electrochemical oxidation with a variety of supporting electrolytes and applied potentials. Pure chemical oxidation was also attempted using ferric chloride. No deposit was obtained in all cases. After stopping the reactions the residue still contained a large amount of the unreacted monomer. However, during both oxidation processes the reaction solution turned slightly blue. This indicates that the monomer may form a very stable radical cation because of delocalisation throughout the phenanthrene ring. With such a high stability it may not readily undergo further reaction. On the other hand, the two extra fused benzene rings may cause steric hindrance to coupling.

#### **3.5.2 Attempt to copolymerise PhITN and ITN**

Whilst PhITN did not undergo polymerisation on its own. It was hoped that the relatively reactive radical cation of ITN may couple with PhITN to form

an ITN-PhITN intermediate which could undergo further reaction to give a copolymer. When the two monomers were used in a 1:1 mole ratio, a blue film was deposited on a Platinum plate working electrode in dichloromethane at 2.0v constant potential, using TBNBr as the supporting electrolyte. The conductivity of the resulting product was very high at  $140 \text{ Scm}^{-1}$ . This was the highest conductivity recorded in this work.

Glc was used to monitor the consumption of the monomers, which showed that both monomers were consumed. However, the consumption of ITN was much faster than that of PhITN. NMR indicated that some of the PhITN monomer remained unreacted but no ITN monomer could be seen after 24 hours of electropolymerisation. The backbone of the resulting polymer probably consists of mainly ITN monomer units with only a few PhITN units. The results do not rule out the possibility that the homopolymer of ITN is formed. We tend to favour the product being a copolymer for two reasons: Firstly the weight of the product is much higher than the starting weight of the ITN monomer even after extensive extraction with dichloromethane for 48 hours. Secondly the resulting blue film was more stable than that of the ITN homopolymer made under the same conditions. However, the precise structure of the product has not been verified, since it was insoluble in most organic solvents.

### **3.5.3 Attempt to polymerise phenanthrenethiophene dicarboxylic acid (PhITNCOOH)**

PhITN was prepared by the sublimation of PhITNCOOH. An attempt was made to directly convert PhITNCOOH to polyPhITN via a Kolbe electrolysis. The Kolbe electrolysis was one of the earliest reactions to be used in organic synthesis which is based on the anodic oxidation of carboxylic acid salts with subsequent decarboxylation and coupling to give a

hydrocarbon dimer<sup>24</sup>. The reaction may involve formation of radical intermediates, which couple with each other to give a dimer.

In this work it was hoped that PhITNCOOH with two carboxylic acid groups would couple to give a dimer with two carboxylic acid groups on each end and further decarboxylation and coupling lead to a long chain polymer of PhITN.

Since PhITNCOOH hardly dissolved in acetonitrile and dichloromethane, dimethylsulfate(DMSO) and N,N-dimethylformamide(DMF) were used as the solvent. No reaction could be observed using a series of supporting electrolytes. The reaction was thus carried out in an aqueous solution of sodium hydroxide and a constant current (10mA/cm<sup>2</sup>) applied in order to ensure a large amount of charge passed through the solution. In sodium hydroxide solution, PhITNCOOH only dissolved if the pH of the solution was higher than 12. However, at this pH no reaction occurred. If sodium hydrogen sulfate was added to this solution to decrease the pH to 8, a reaction was observed. Further reduction of the pH led to precipitation of the PhITNCOOH. At pH 8 a slightly yellow deposit was formed on the Platinum working electrode and the colour extended to the top of the solution. When the pH increased to 10 the reaction ceased and no further deposit was formed. After re-addition of sodium hydrogen sulfate to adjust the pH back to 8 the deposit was formed again. At first it was thought that the deposit may be a polymer. However, it is more likely that the product is the mono carboxylic acid of PhITN formed by the decarboxylation of PhITNCOOH. The product was examined using FT-IR which showed a strong carbonyl peak with a position slightly shifted from that in the starting material. One reason why anodic electrolysis of PhITNCOOH leads to the mono carboxylic acid of PhITN rather than a polymer may be that the



resulting radical intermediate is stable and undergoes a disproportionation reaction.

### **3.6 Attempt to Prepare Polyisothianaphthene from Thiophthalide**

An attempt was made to convert thiophthalide into polyisothianaphthene via an aldol type condensation. First, we attempted to use trimethylchlorosilane to produce a trimethylsilyl enol ether<sup>25,26</sup>, followed by a Lewis acid catalysed aldol reaction. Unfortunately, the carbonyl group of the thiophthalide did not readily undergo enolisation with trimethylchlorosilane. We also tried a strong base catalysed aldol reaction<sup>27</sup> using methyllithium, butyllithium and lithium diisopropylamide(LDA). However, we were not successful in each case. After work up, the desired polymer was not obtained and the starting material, thiophthalide, still remained. Despite these results we still consider the conversion of thiophthalide into polyisothianaphthene a very attractive pathway to produce a highly conjugated polymer without defects, and more work needs to be carried out on this system in the future.

### **3.7 Attempt to Prepare Polysilole from 1,1,3,4-Tetramethyl-1-silacyclopent-3-ene and 1,1,3,4-Tetramethylsilacyclopentadiene**

Weber and coworkers<sup>28,29</sup> have recently reported that silacyclopent-3-enes undergo a ring-opening polymerisation which is catalysed by alkylolithium reagents, to yield linear polysila-*cis*-pent-3-enes together with dimers. They have proposed a mechanism for this anionic ring opening polymerisation which involves attack of a carbanion on the silicon to form a hypervalent pentacoordinate silicon species. Ring opening of this hypervalent anion gives a *cis*-allyl anion which attacks another molecule of 1-silacyclopent-3-ene, thus, forming another hypervalent silicon intermediate. In this work we examined ways of preparing polysiloles from 1,1,3,4-tetramethyl-1-sila-3-

cyclopentene(TMSCP) and 1,1,3,4-tetramethylsilacyclopentadiene (TMSCPD) by electrolysis and chemical polymerisation.

### **3.7.1 Electrochemical oxidation**

We tried to polymerise TMSCPD and TMSCP using the electrochemical techniques previously used for polymerisation of isothianaphthenes.

Irrespective of the reaction conditions (applied potentials, reaction times, solvents and supporting electrolytes), no colour change was observed in the solution. No polymer was formed. After work up, most of the monomer remained. We found that when the potential was applied, a very thin film was deposited on the working electrode. This led to a sharp drop in current such that further reaction stopped.

### **3.7.2 Chemical polymerisation**

No polymerisation of TMSCPD or TMSCP occurred in the presence of catalytic amounts of n-butyllithium, methyllithium or benzoyl peroxide in THF or hexane. The monomer remained after 48 hours together with some soluble, unidentified byproducts.

## **3.8 Characterisation of Isothianaphthene Polymers**

### **3.8.1 Polymers prepared from DMITN and DMDHITN**

#### **1) FT-IR**

The FT-IR spectra of poly(5,6-dimethylisothianaphthene) (PDMITN) formed from DMITN and DMDHITN are shown in Figure 3-10 a-d with the assignments listed in Table 3-3. The spectrum of the DMITN monomer is reported for comparison. It was noted that the spectra of the four polymer samples are similar. Sample a and b were made from DMITN and DMDHITN by electrolysis in the presence of TBNBr at 2.0v vs. Ag/AgCl.

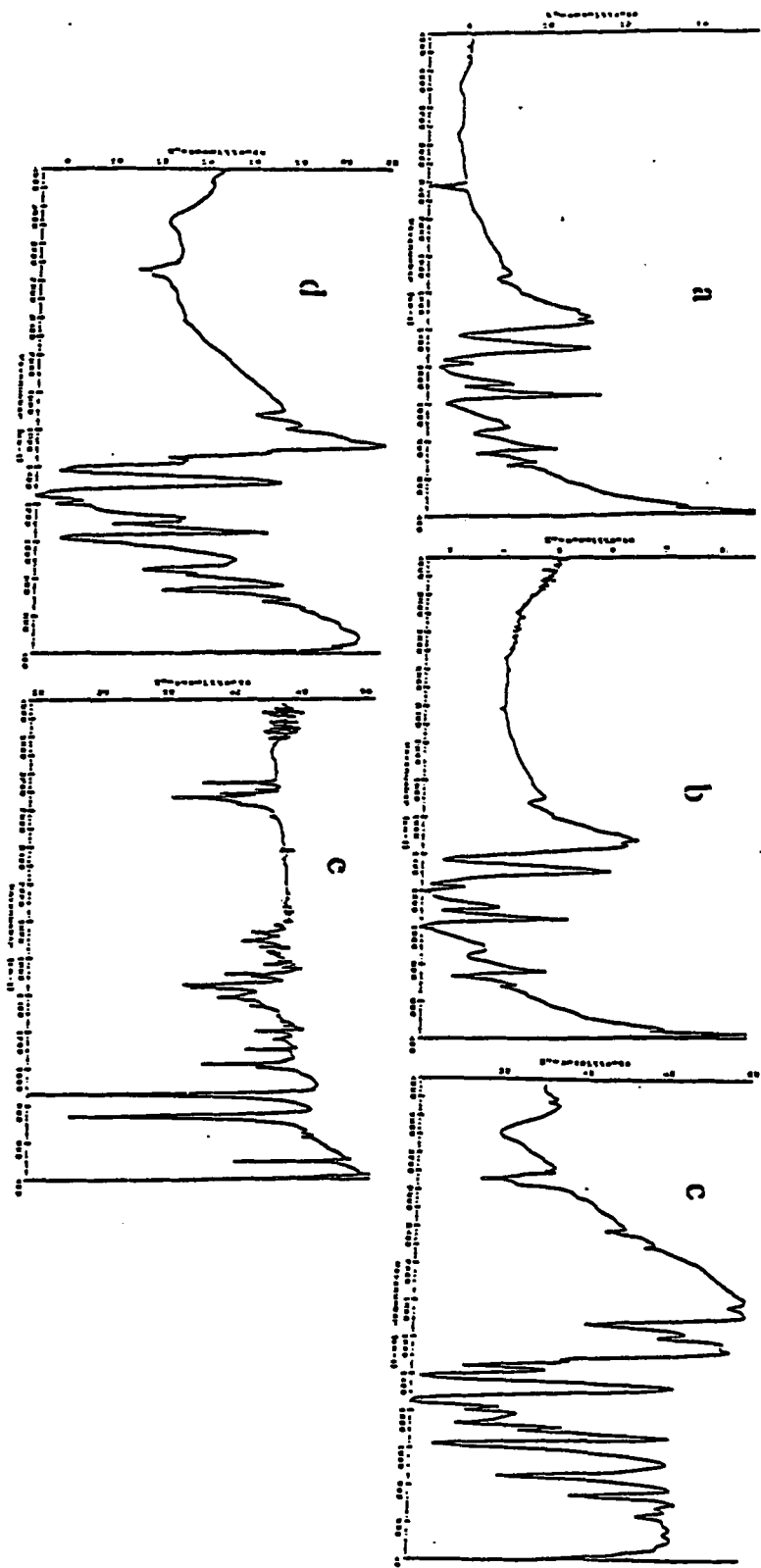


Figure 3-10 FT-IR spectra of PDMITN obtained using different conditions. a) and b) made from DMITN and DMDHITN by electrolysis at 2.0v in the presence of TBNBF, c) made from DMITN by electrolysis at 2.0v in the presence of TENBF, d) made from DMITN by chemical oxidation with ferric chloride and e) DMITN monomer.

They both have very strong absorbances in the region from 4000 to 2000  $\text{cm}^{-1}$  such that the absorption peaks due to the aliphatic C-H stretching( $-\text{CH}_3$ ) are overshadowed. In samples c and d the absorption peaks of methyl C-H stretch are clearly seen.

The absorbances which arise from the thiophene ring in both the polymer and the monomer occur in the vicinity of 1500-1100  $\text{cm}^{-1}$  and are quite clearly seen (normally four bands for the parent thiophene<sup>30</sup>). Two strong bands at about 850 and 730  $\text{cm}^{-1}$  were also observed in the spectrum of all the samples, including the monomer, and correspond to the aromatic out of plane C-H deformation and ring out of plane vibration. The peak at 740  $\text{cm}^{-1}$  also appear in the spectrum of the unsubstituted polymer, PITN<sup>31</sup>, as well as in substituted thiophene<sup>32</sup> and polythiophene<sup>33</sup>. These observations confirm that the new polymer, PDMITN, contains the intact isothianaphthene ring structure.

Table 3-3 FT-IR absorbances and assignments for PDMITN

| Sample No | Aromatic C-H stretching | Aliphatic C-H stretching | Thiophene ring stretching    | Aromatic out of plane C-H deformation and ring out of plane vibration |
|-----------|-------------------------|--------------------------|------------------------------|---|
| DMITN     | 3089, 3019, 2975        | 2933, 2912, 2854         | 1440, 1433, 1381, 1333, 1199 | 858, 740  |
| Sample a  | 2965,2958               | 2918, 2886, 2856         | 1446,1364, 1235, 1198        | 841, 734  |
| Sample b  | —                       | —                        | 1450, 1438, 1238, 1200       | 844, 737  |
| Sample c  | 3120, 3112, 3010, 2963  | 2915, 2888, 2859         | 1480, 1448, 1391, 1252, 1206 | 848, 742  |
| Sample d  | 3089, 3019, 2975        | 2932, 2915, 2886, 2857   | 1448, 1394, 1225, 1204       | 849, 737  |

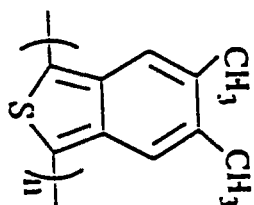
## 2) $^{13}\text{C}$ CP/MAS NMR

The solid state  $^{13}\text{C}$  CP/MAS NMR spectra of the polymer are shown in Figures 3-11 and 12. The two samples were made from DMITN by electrolysis at 2.0v in the presence of either TENBF or TBNBr. The  $^{13}\text{C}$  NMR spectrum in Figure 3-11 was recorded directly. The spectrum in Figure 3-12 was obtained after the sample had been dedoped with aqueous  $\text{NH}_3$  for 24 hours, since its high conductivity (5.0 s/cm in the oxidised state) affects the NMR signal. Comparison of two spectra shows that both have strong peaks at 19-20 ppm and 126 ppm. These correspond to the methyl groups and the hydrogens in the fused benzene ring. The first sample which has a poor conductivity, has an extra broad peak at 58 ppm corresponding to a protonated carbon. This indicates the presence of saturated carbon defects in the backbone of the polymer or short chain polymers with a relatively high proportion of terminal hydrogens. The defects seem to result from the disproportionation and transformation of the intermediate species (including radical cations and neutral product) in solution during the polymerisation. The weak intensity of the peak at 58 ppm suggests that poly(1,3-dihydroisothianaphene) was not formed.

## 3) Elemental analysis

The elemental analyses of PDMITN made from DMITN and DMDHITN under different conditions are listed in Table 3-4. These results confirm that sulphur remains in the polymer and the isothianaphthene ring is not broken during the polymerisation. Furthermore, the total percentage of the three elements C, H and S is below 100% so there must be either some anions of the electrolytes ( $\text{BF}_4^-$ ,  $\text{Br}^-$  or  $\text{FeCl}_4^-$ ) remaining in the polymer, or the polymer is over-oxidised or traces of water remain in the samples.

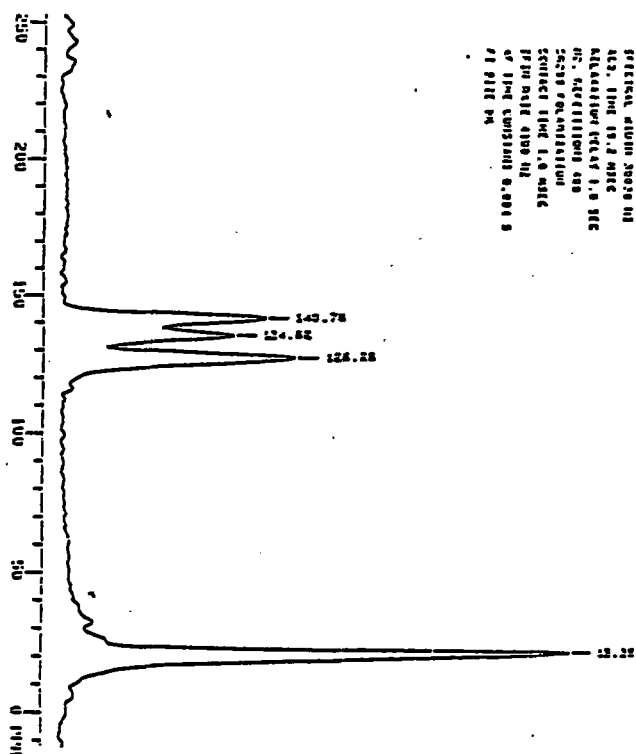




Protonated  
carbon

CPMAS  
Date: 02-07-03  
Time: 15.20  
File: 02-07-03  
Name: 02-07-03

CPMAS  
Date: 02-07-03  
Time: 15.20  
File: 02-07-03  
Name: 02-07-03  
Date: 02-07-03  
Time: 15.20  
File: 02-07-03  
Name: 02-07-03



Non-protonated  
carbon

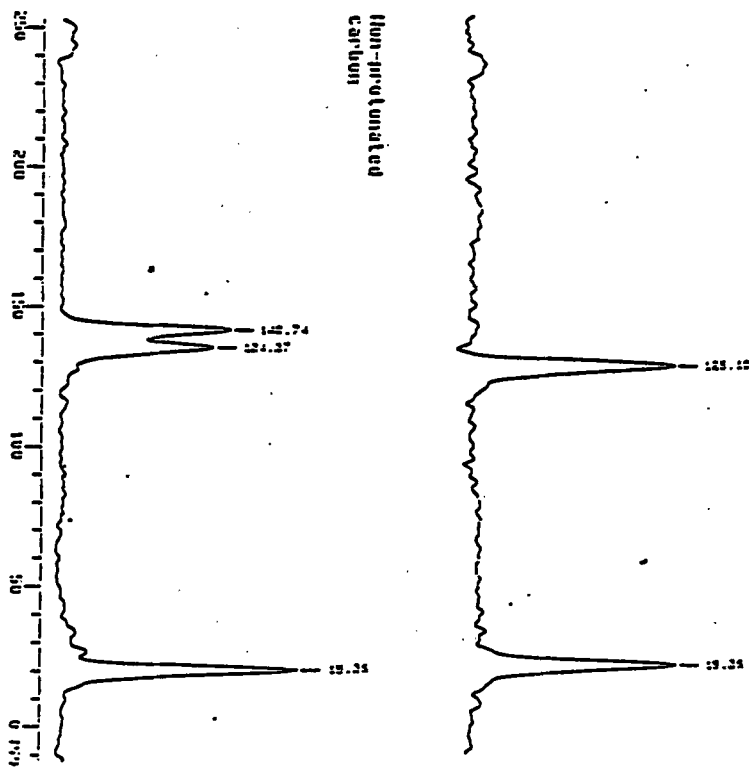


Figure 3-12  $^{13}\text{C}$  CP/MAS NMR spectra of PDMITN made by electrolysis of DMITN at 2.0V in the presence of TBNBr.

Table 3-4 Summary of the elemental analysis of PDMITN\*

| Element | C       | H     | S      |
|---------|---------|-------|--------|
| Theory  | 75%     | 5%    | 20%    |
| A       | 69.35%  | 4.96% | 18.45% |
| B       | 70.89 % | 4.90% | 18.36% |
| C       | 71.56%  | 5.10% | 18.57% |
| D       | 68.00%  | 4.91% | 18.18% |

\*Note: The samples are the same as those used in FT-IR.

#### 4) UV/Vis-near IR

Electron absorption spectra (UV/Vis-near IR) were obtained for polymers with different conductivities as listed in Table 3-5. The sample with a conductivity of over  $10^{-1} \text{ Scm}^{-1}$  shows a strong absorption peak at about 840 nm and two long wavelength peaks in the near IR region ( 1300 and 1650 nm). The sample with a conductivity of about  $10^{-2} \sim 10^{-3} \text{ Scm}^{-1}$  shows a strong peak at 690 nm and two long wavelength peaks at 1330 and 1660 nm respectively. However, the sample with a conductivity of about  $10^{-5} \text{ Scm}^{-1}$  displays a strong peak at 525 nm and a broad weak peak at 1320 nm. The first strong peak in each case indicates that the conducting polymer has a relatively long conjugated chain the longer the wavelength the more extensive the conjugation. The two peaks in the near IR region correspond to radical cations and dications of the polymer. In all of the three spectra, the onset of the first absorption peak ( onset of the  $\pi-\pi^*$  transition) was at the same position corresponding to a transition of 1.1ev. This could be considered as the band gap of PDMITN. This indicates that the introduction of methyl groups does not substantially affect the band gap of the isothianaphthene polymer. The spectra are very similar to those of the parent polyisothianaphthene reported by Onoda<sup>34</sup> and Gumbs<sup>14</sup>.



Table 3-5 Summary of UV/Vis. near IR absorption peaks( $\lambda_{\max}$ ) of PDMITN

| Sample No | first peak | second peak | third peak | conductivity               |
|-----------|------------|-------------|------------|----------------------------|
| A         | 840nm      | 1300nm      | 1650nm     | $10^{-1} \text{ Scm}^{-1}$ |
| B         | 690nm      | 1330nm      | 1660nm     | $10^{-3} \text{ Scm}^{-1}$ |
| C         | 525nm      | 1320nm      |            | $10^{-5} \text{ Scm}^{-1}$ |

### 5) X-ray powder diffraction

X-ray diffraction patterns of PDMITN made under different conditions are shown in Figure 3-13. The characteristic angles at intensity maxima and the corresponding values of the spacings,  $d$ , calculated using Bragg's law( $d = \lambda / 2\sin\theta$ ) are listed in Table 3-6.

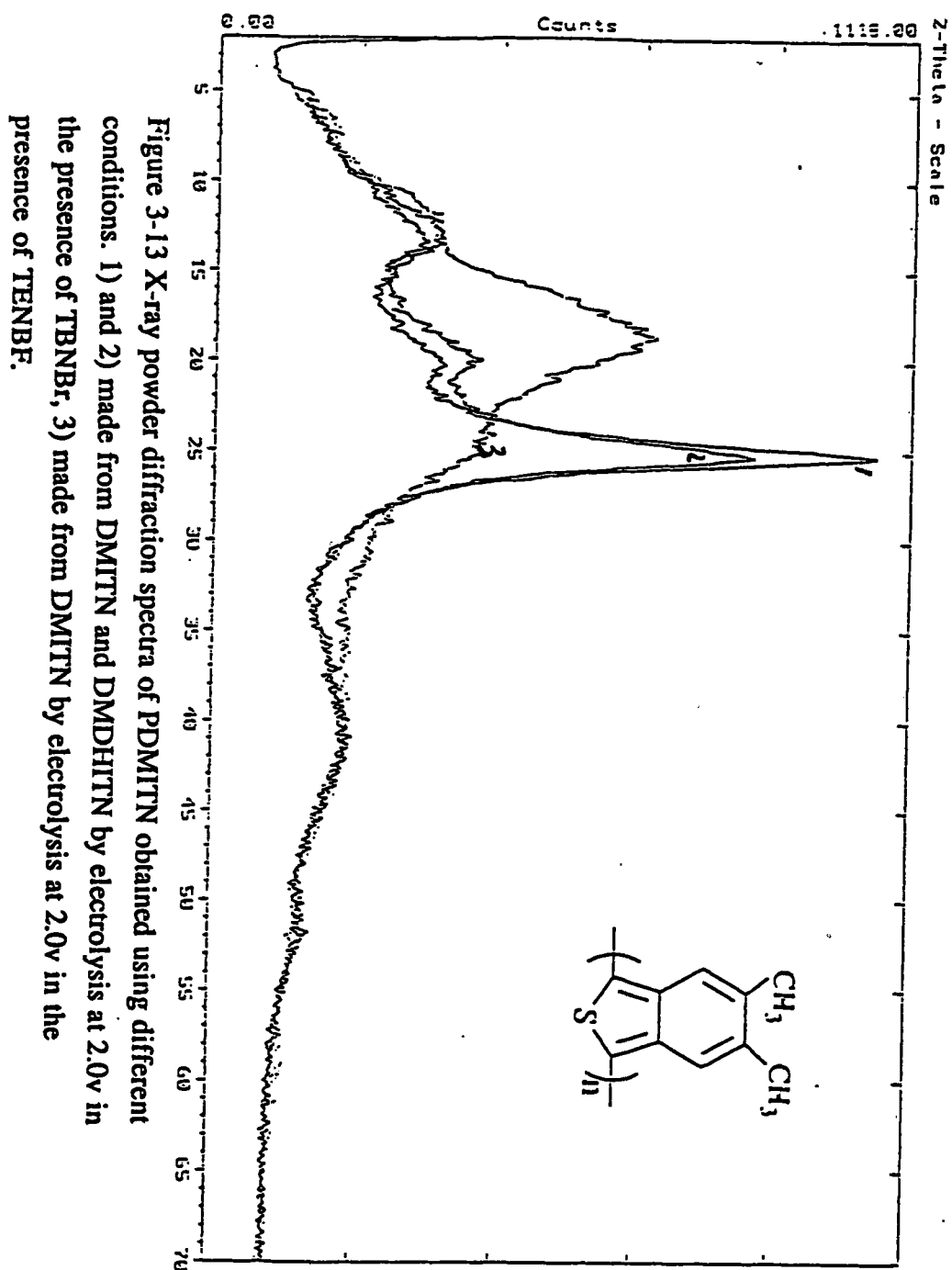
All three samples had a range of diffuse peaks with intensity maxima at the same positions of  $14^\circ$ ,  $20^\circ$ ,  $25^\circ$ ,  $40^\circ$  and  $52^\circ$  ( $2\theta$ ) even though the polymers were obtained under different conditions. This indicates that the three samples are similar, that is the same type of polymer(PDMITN) is obtained in all cases. Curves one and two are nearly identical even though sample one was made from DMITN whilst sample two was made from DMDHITN.

Table 3-6 X-ray diffraction maxima and  $d$  spacing of PDMITN

| Sample No    | $2\theta(\text{degree})/d \text{ spacing}(\text{\AA})$ |        |        |        |        |
|--------------|--|--------|--------|--------|--------|
|              | first  | second | third  | fourth | fifth  |
| sample one   | 14/6.3   | 20/4.4 | 25/3.6 | 40/2.3 | 52/1.8 |
| sample two   | 14/6.3   | 20/4.4 | 25/3.6 | 40/2.3 | 52/1.8 |
| sample three | 14/6.3   | 20/4.4 | 25/3.6 | 40/2.3 | 52/1.8 |

However, there were differences between curves three and one(or two).

Samples one and two with high conductivity, made in the presence of TBNBr, have a very strong, sharp diffuse peak at  $25^\circ$ . The peak intensity at  $25^\circ$  for sample three, a poor conductor, made in the presence of TENBF, is very weak. Nevertheless, the amorphous phase seemed to predominate in all of these samples. The samples with a strong and sharp peak at  $25^\circ$  could have relatively high one dimensional order. The UV/Vis near IR results



indicate that the highly conducting polymers have a long conjugated chain which may lead to this high intensity peak at  $25^{\circ}$ . In contrast, the sample with shorter conjugated chains would have a smaller peak intensity at  $25^{\circ}$  as observed in sample three.

The peak at  $14^{\circ}$  may arise from a disordered phase and the peak at  $20^{\circ}$  from interplanar spacing, with a broad distribution resulting from the presence of methyl groups, as in the case of poly(3-methylthiophene) reported by Chen<sup>35</sup>. The weak and broad peaks at wide angles of  $40^{\circ}$  and  $52^{\circ}$  are also found in all three samples. Comparison with the diffraction pattern of poly(3-alkylthiophene)<sup>36</sup>, suggests that these peaks are not related to the internal structure of the isothianaphthene molecule but indicate the presence of relatively straight polymer chains in a predominately amorphous polymer product. If the conjugated chain of the polymer was long enough and the interchain order was relatively high, the wide angle peaks would become strong and sharp.

### **3.8.2 Polymers prepared from ITN and DHITN**

#### **1) FT-IR**

The FTIR spectra of polyisothianaphthene(PITN) made from ITN and DHITN respectively are shown in Fig. 4-14a-d with the assignment listed in Table 3-7. The spectrum of the ITN monomer was reported for comparison. The spectra of the four polymer samples are similar. Samples a and b were obtained from ITN and DHITN by electrolysis at 2.0v in the presence of TBNBr. Sample c was made from ITN in the presence of TENBF by electrolysis at 2.0v and sample d was made from ITN by pure chemical oxidation with ferric chloride. The broad absorbance over  $2000\text{ cm}^{-1}$  prevented the observation of the C-H stretching bands.

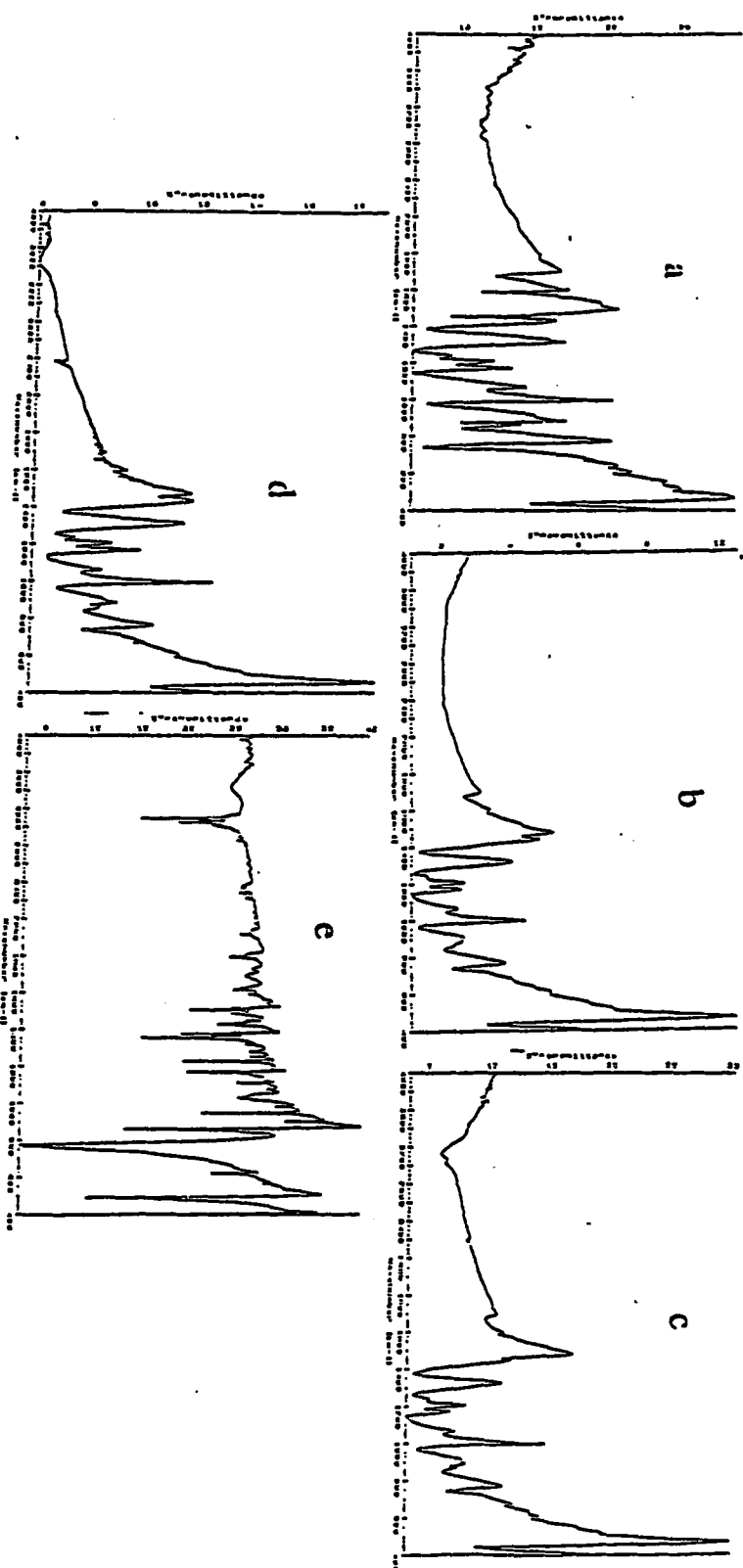


Figure 3-14 FT-IR spectra of PITN obtained using different conditions.

a) and b) made from ITN and DHITN by electrolysis at 2.0v in the presence of TBNBr respectively, c) made from ITN by electrolysis at 2.0v in the presence of TENBF, d) made from ITN by chemical oxidation with ferric chloride and e) ITN monomer.

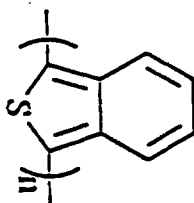
Nevertheless, the absorption bands arising from the isothianaphthene ring for both the polymer and the monomer at 1500-1100  $\text{cm}^{-1}$  were present. The bands were approximately in the same positions in all of the polymer samples. An absorption band at 730  $\text{cm}^{-1}$  corresponding to the C-H out-of-plane vibration of the polyisothianaphthene was observed in all cases. These are consistent with the spectra reported by Higgins<sup>37</sup> and Wudl<sup>31</sup>. It appears that the structure of the polymer is the same irrespective of how the polymers were prepared.

Table 3-7 FT-IR absorbances and assignments for PITN

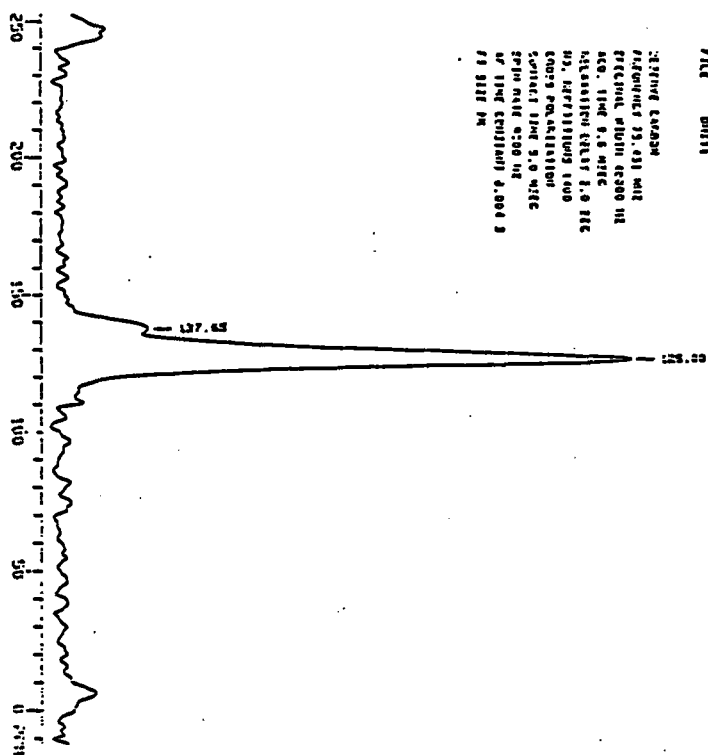
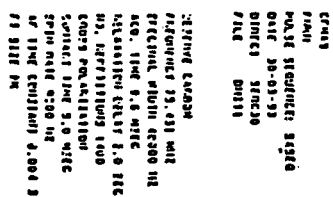
| Sample No | Aromatic C-H stretching | Thiophene ring stretching          | Aromatic out of plane C-H deformation and ring out of plane vibration |
|-----------|-------------------------|------------------------------------|---|
| ITN       | 3092, 3051, 3025        | 1505, 1427, 1372, 1352, 1225, 1164 | 950, 856, 775   |
| Sample a  | —                       | 1451, 1381, 1264, 1222, 1141       | 973, 840, 738   |
| Sample b  | —                       | 1449, 1384, 1265, 1217, 1140       | 969, 838, 736   |
| Sample c  | —                       | 1450, 1374, 1260, 1228, 1141       | 965, 841, 738   |
| Sample d  | —                       | 1451, 1373, 1260, 1214, 1136       | 960, 835, 734   |

## 2) $^{13}\text{C}$ CP/MAS NMR

The solid state  $^{13}\text{C}$  CP/MAS NMR of the polymers are shown in Figures 3-15 and 16. The first sample, Figure 3-15, was made from DHITN by electrolysis at 2.0v in the presence of TBNBr. The second sample, Figure 3-16, was made from ITN by electrolysis at 2.0v in the presence of TENBF. The former, with a higher conductivity, needed to be dedoped with aqueous ammonia for 24 to decrease the conductivity below  $10^{-3} \text{ Scm}^{-1}$ , before it could be tested by NMR. The spectrum of the second sample could be recorded directly owing to its poor conductivity. In both spectra two non-



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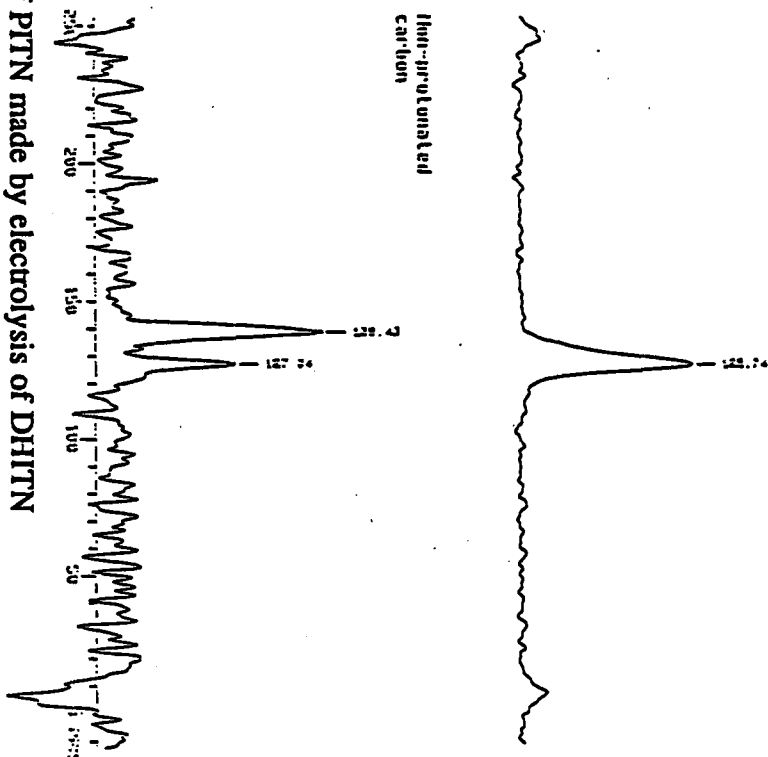
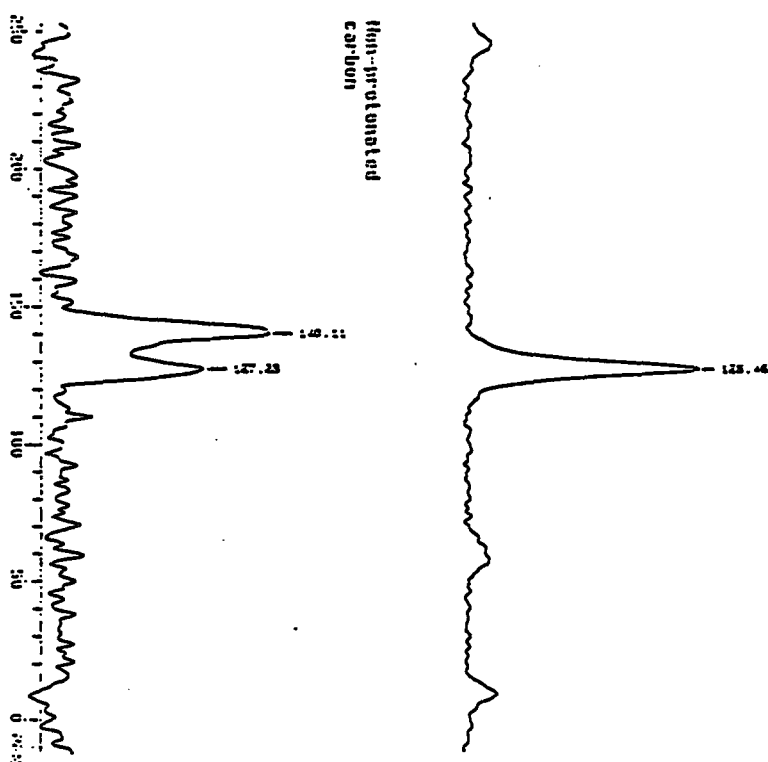
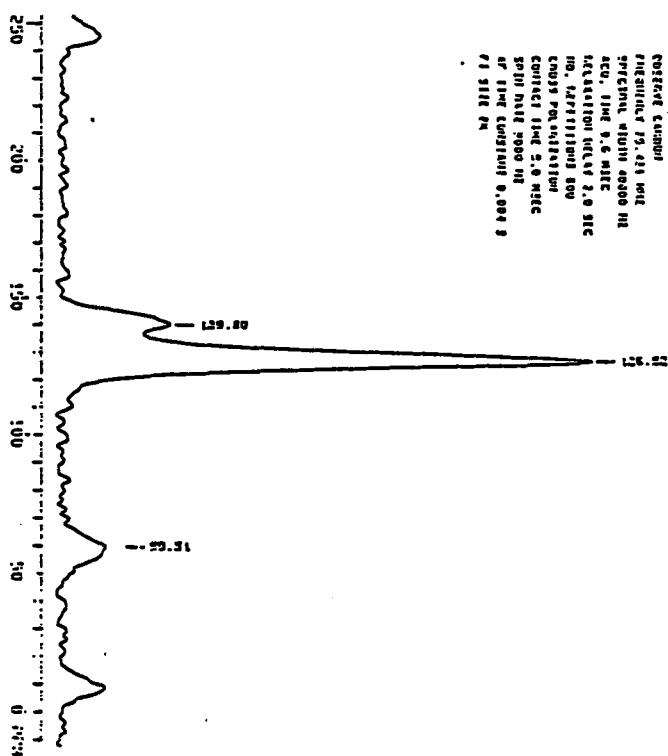
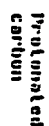


Figure 3-15  $^{13}\text{C}$  CP/MAS NMR spectra of PITN made by electrolysis of DHITN at 2.0V in the presence of TBNBr.



**Figure 3-16  $^{13}\text{C}$  CP/MAS NMR spectra of PITN made by electrolysis of ITN at 2.0V in the presence of TENBF.**

protonated carbon peaks could be seen at 140-138 ppm and 127 ppm corresponding to C<sub>3</sub> and C<sub>3a</sub> respectively. One protonated carbon peak was seen at 125-126 ppm. It seems that the signals arising from C<sub>4</sub> and C<sub>5</sub> could not be separated. These results are in agreement with those reported by Hoogmartens<sup>38</sup>. The polymer (Sample one) directly formed from DHITN did not show a peak at 59ppm, however, the polymer formed from ITN had a peak at 59 ppm arising from saturated C-H defects along the polymer chain. This confirms that DHITN, the 1,3-dihydro compound, could be converted to a conjugated polymer without C-H defects in the main chain. Clearly, the formation of long conjugated chain polymer is more dependent on the external reaction conditions than the choice of monomers.

### 3) Elemental analysis

The elemental analysis of PITN formed from ITN and DHITN under different conditions are listed in Table 3-8. The samples selected are the same as those used in FT-IR testing. These results confirm that sulphur remains in the polymer and the isothianaphthene ring is not broken during the polymerisation. The total percentage of C, H and S is not 100%, indicating that either some anions of the electrolytes (BF<sub>4</sub><sup>-</sup>, Br<sup>-</sup> or FeCl<sub>4</sub><sup>-</sup>) remain in the polymer, or the polymer is over-oxidised, or traces of water remain in the samples.

Table 3-8 Summary of the elemental analysis of PITN\*

| Element | C       | H     | S      |
|---------|---------|-------|--------|
| Theory  | 72.73%  | 3.03% | 24.24% |
| A       | 67.62%  | 3.28% | 22.45% |
| B       | 68.03 % | 3.32% | 22.87% |
| C       | 67.98%  | 3.21% | 21.67% |
| D       | 66.68%  | 3.16% | 20.47% |

\*Note: The samples are the same as those used in FT-IR testing.



#### 4) UV/Vis-near IR

Electronic spectra(UV/Vis-near IR) were obtained for three powder samples of PITN with conductivities of  $10^1$ ,  $10^{-2}$ , and  $10^{-4}$  Scm $^{-1}$ . These are shown in Figure 3-17. The spectra are similar to those of PDMITN discussed earlier. The sample with the higher conductivity shows a strong  $\pi$ - $\pi^*$  transition absorption at about 830 nm and two strong longer wavelength peaks in the near IR region at about 1310 and 1640 nm. The sample with medium conductivity shows a strong  $\pi$ - $\pi^*$  transition absorption at 710 nm and two long wavelength peaks at about 1340 nm and 1600 nm. But the sample with poor conductivity displays a strong  $\pi$ - $\pi^*$  transition absorption at 550 nm and a weak broad long wavelength peak at about 1350 nm.

The onset of the  $\pi$ - $\pi^*$  transition absorption band in the three spectra were all located at roughly the same wavelength corresponding to 1.1ev, which represents the band gap of the resulting polymer. The two long wavelength peaks in the near IR region are attributed to the radical cation and dication of the resulting polymer in the oxidised state. These results are consistent with those reported by Wudl<sup>39</sup> and Onoda<sup>34</sup>, who obtained the optical absorption spectra of a PITN thin film, in situ during electrochemical doping. They found that PITN had a single peak at about 800 nm due to interband excitation in the undoped state, and as the doping proceeded, a new absorption peak built up at about 1500 nm.

#### 5) X-ray powder diffraction

X-ray diffraction patterns of PITN made under different conditions are shown in Figure 3-18, and the characteristic angles at intensity maxima and the corresponding spacings,  $d$ , calculated using Bragg's law are listed in Table 3-9.

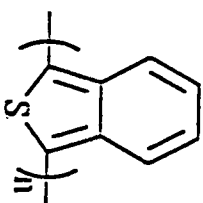
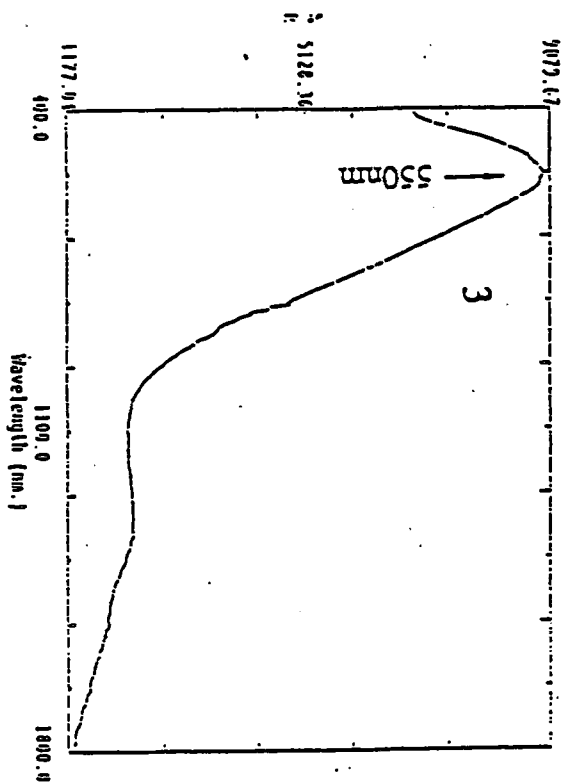
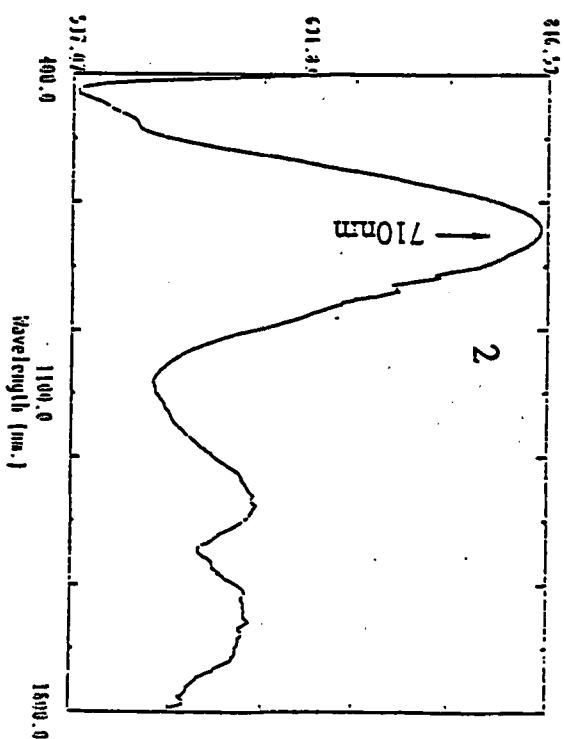
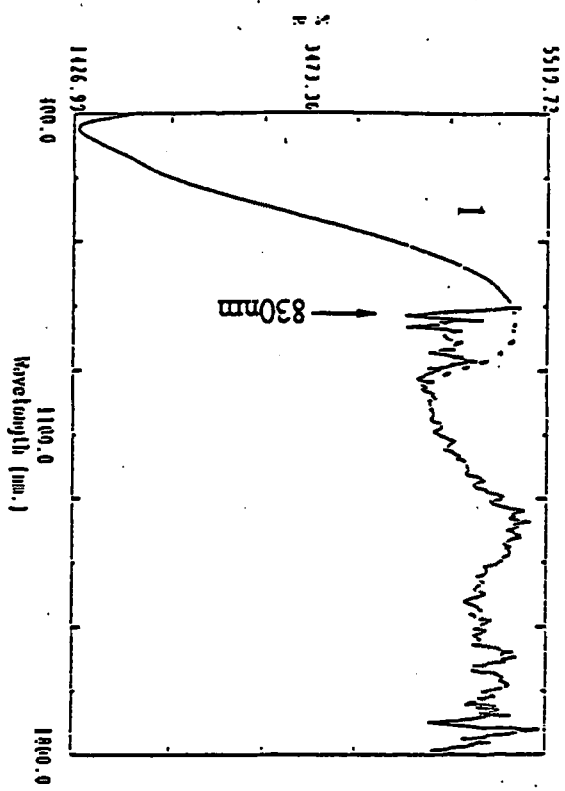


Figure 3-17 UV/Vis.-near IR spectra of PTN with different conductivities. 1)  $\sim 10$  s/cm, 2)  $\sim 10^{-2}$  s/cm and 3)  $\sim 10^{-4}$  s/cm

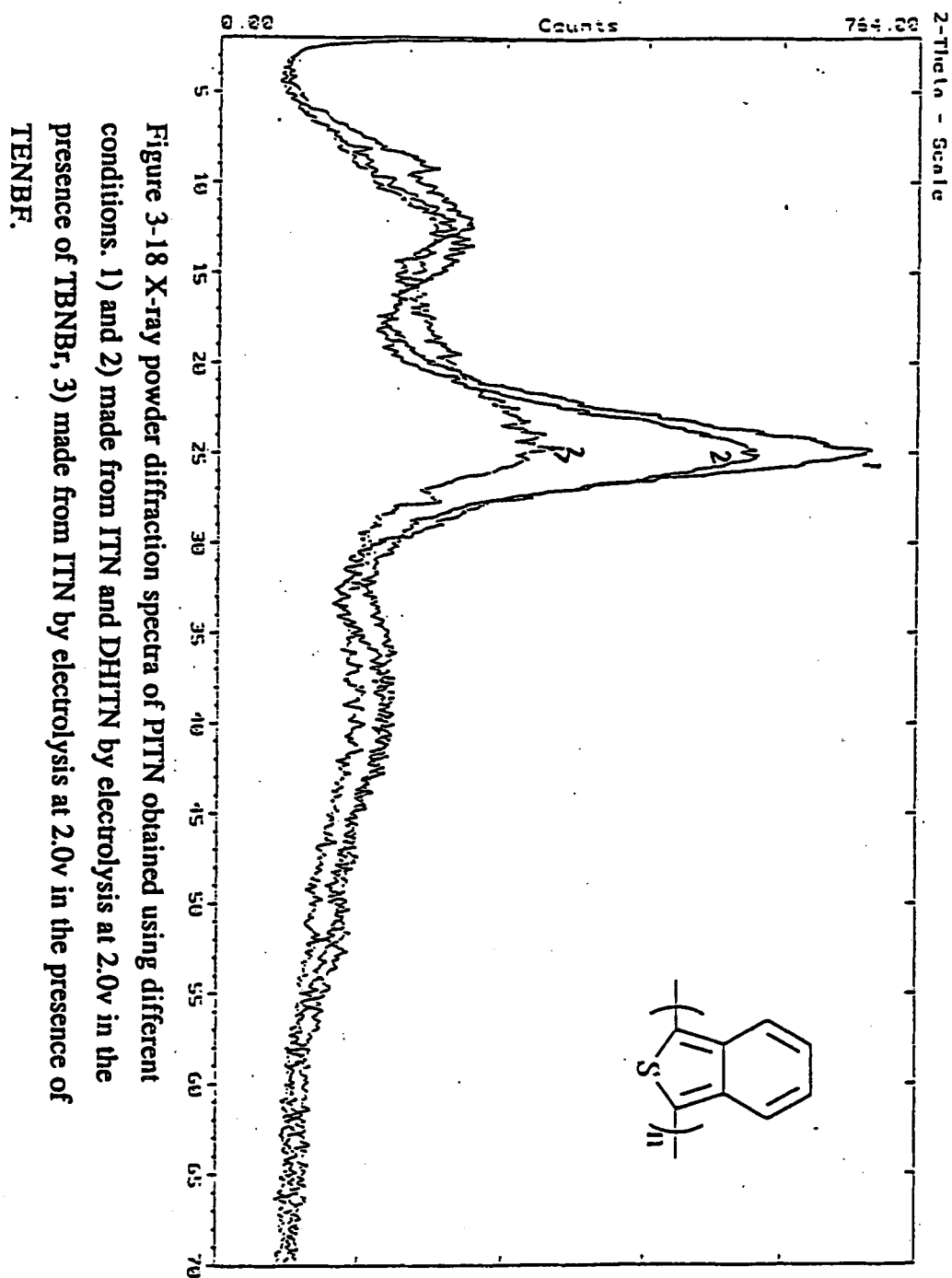
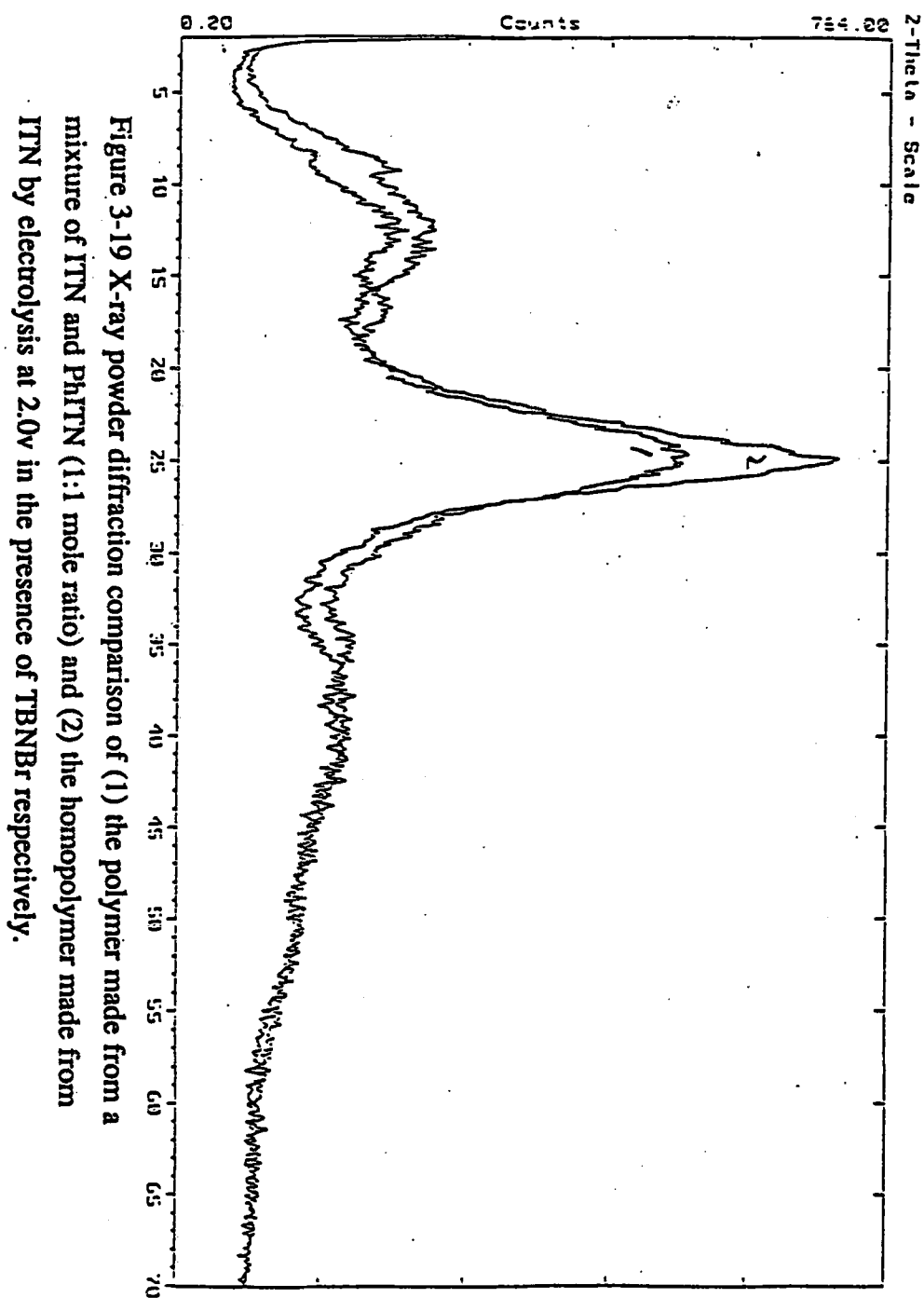


Figure 3-18 X-ray powder diffraction spectra of PTN obtained using different conditions. 1) and 2) made from ITN and DHITN by electrolysis at 2.0v in the presence of TBNBr, 3) made from ITN by electrolysis at 2.0v in the presence of TENBF.

Table 3-9 X-ray diffraction maxima and d spacing of PITN

| Sample No    | 2 $\theta$ (degree)/d spacing(A) |        |        |        |
|--------------|----------------------------------|--------|--------|--------|
|              | first                            | second | third  | fourth |
| sample one   | 14/6.3                           | 25/3.6 | 40/2.3 | 52/1.8 |
| sample two   | 14/6.3                           | 25/3.6 | 40/2.3 | 52/1.8 |
| sample three | 14/6.3                           | 25/3.6 | 40/2.3 | 52/1.8 |

The three samples all had a range of diffuse peaks with maximal intensities at roughly the same positions; 14 $^{\circ}$ , 25 $^{\circ}$ , 40 $^{\circ}$ , and 54 $^{\circ}$  (2 $\theta$ ), even though the polymer samples were obtained under different conditions. The spectra of the three samples are identical. This indicates that they are the same polymer(PITN). Curve one and two are very similar even though sample one is made from ITN and sample two is made from DHITN. However, the spectrum of sample three made from ITN in the presence of TENBF is different from that of sample one and two. The diffuse peak at 25 $^{\circ}$  is very broad and weak in sample three. As discussed for the PDMITN system, the polymer made in the presence of a nucleophilic electrolyte, TBNBr, with a high conductivity has a strong peak at 25 $^{\circ}$ . The peak shape at 25 $^{\circ}$  is not dependent on the conductivity itself but dependent on the conjugated chain structure of the polymer, since the sharp peak at 25 $^{\circ}$  is not affected by the undoping process. That is, the spectra of the polymer in both undoped and doped states show the same characteristics. Thus, this peak is considered to correspond to the conjugated chain and interchain order of the polymer. This strong peak at 25 $^{\circ}$  is consistent with the electron and x-ray diffraction results reported by Yashima and coworkers<sup>40</sup>. They compared the electron micrograph and x-ray spectra of PITN and concluded that this strong peak is not associated with the PITN repeat unit since the d-spacing(3.53Å) of this peak is much smaller than that of the repeat unit along the polymer chain(about 8Å). This indicates that this peak corresponds to an interchain stacking.



As in the PDMITN system, the peak at  $14^{\circ}$  may arise from the disordered phase. The weak and broad peaks at larger angles of  $40^{\circ}$  and  $52^{\circ}$  are not related to the internal structure of the isothianaphthene molecules but correspond to relatively straight polymer chains in a predominantly amorphous product.

Comparison of these spectra with those of PDMITN shows one peak at  $20^{\circ}$  which was present with PDMITN but not with PITN. This peak is probably a result of the methyl substituents. The 'copolymer' made from ITN and PhITN (1:1 in mole ratio), in the presence of TBNBr, has a spectrum which is slightly different to that of the ITN homopolymer as shown in Figure 3-19. There are two extra peaks at  $17^{\circ}$  and  $35^{\circ}$  respectively. This may be related to the introduction of the PhITN unit into the polymer.

### **3.8.3 Polymer prepared from MeODHITN**

FT-IR,  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR, X-ray powder diffraction as well as gel permeation chromatography were used to characterise the reduced form of the polymer made from MeODHITN by electrolysis at 2.0v in the presence of TENBF.

#### **1) FT-IR**

The FT-IR spectrum of PMeOITN is shown in Figure 3-20 together with the spectrum of the monomer, MeODHITN. The polymer had peaks at 3010, 2930 and  $2830\text{ cm}^{-1}$  corresponding to the C-H stretching of the benzene ring and aliphatic C-H stretching. The strong peak at  $1262\text{ cm}^{-1}$  could be assigned to the C-O-C stretching of the methoxy group. As with the PDMITN and PITN systems, the peaks at 1584, 1530, 1469 and  $1437\text{ cm}^{-1}$  could be associated with the isothianaphthene ring vibration.

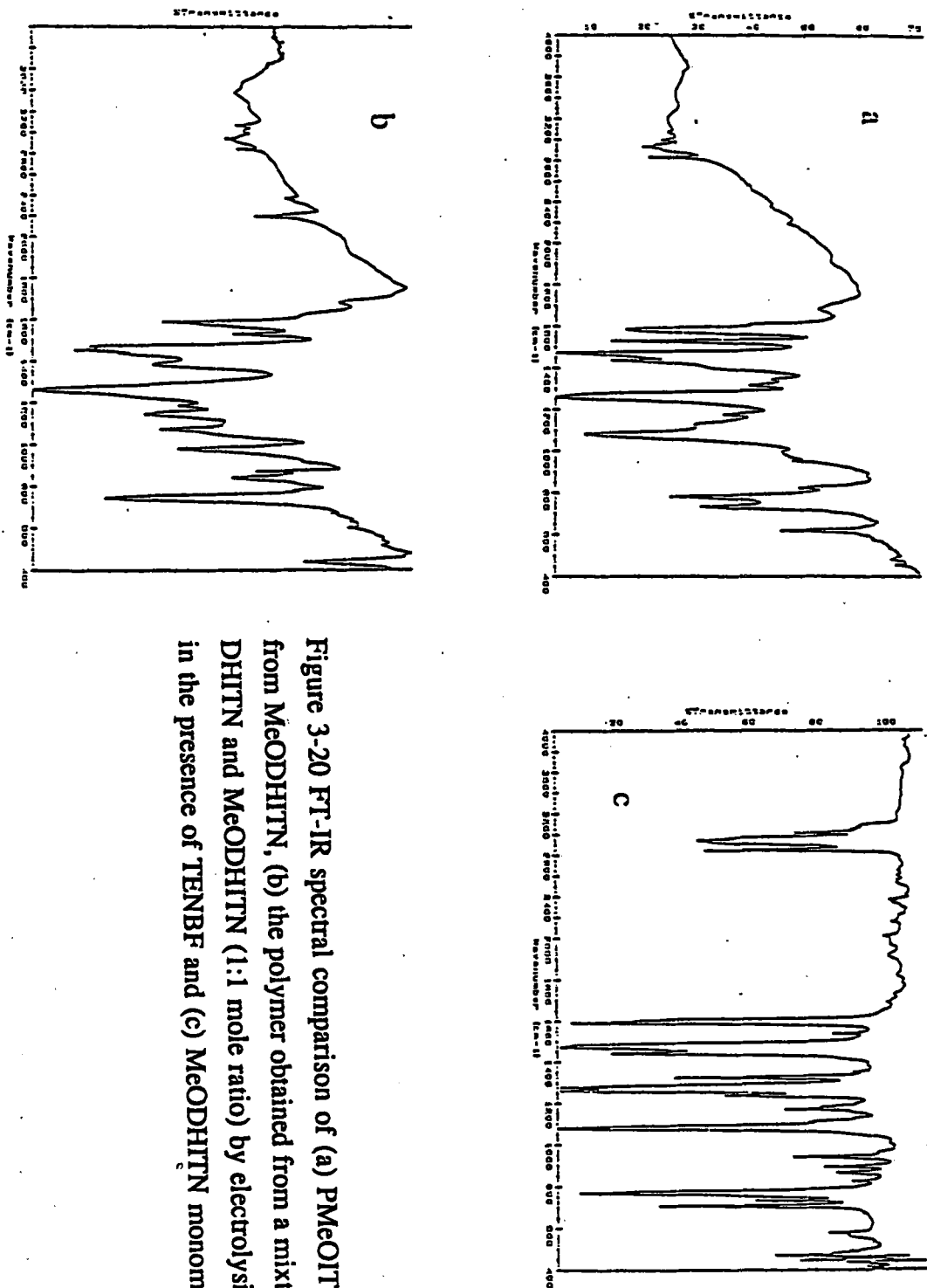


Figure 3-20 FT-IR spectral comparison of (a) PMeODITN made from MeODHITN, (b) the polymer obtained from a mixture of DHITN and MeODHITN (1:1 mole ratio) by electrolysis at 2.0V in the presence of TENBF and (c) MeODHITN monomer.

The spectrum of the polymer made from a mixture of MeODHITN and DHITN by electrolysis is also reported in Figure 4-20(b). The spectrum is different from both the spectra of PMeOITN and PITN. The spectrum of the polymer shows characteristics of both homopolymers (see Figure 3-14 and Table 3-6). Besides the peaks at 3010, 2931, 2826, 1587, 1529, 1471, 1437 $\text{cm}^{-1}$  related to the repeat unit of PMeOITN, the peaks at 3059, 1452, 1384, 1145, 979 and 840  $\text{cm}^{-1}$  are associated with the repeat unit of PITN.

## 2) $^1\text{H}$ and $^{13}\text{C}$ solution NMR

Since the polymer easily dissolved in dichloromethane and chloroform the  $^1\text{H}$  and  $^{13}\text{C}$  solution NMR of PMeOITN were obtained in deuterated chloroform and the spectra are shown in Figure 3-21. The assignment of the peaks in the spectrum is straightforward. The  $^1\text{H}$  NMR spectrum shows a strong peak at 4ppm corresponding to the methoxy protons and three broad peaks in the range 6 to 8ppm arise from the protons on the aromatic ring. It was noted that the integration ratio of the aromatic protons to those of the methoxy group was almost one. There was no peak between 4ppm and 6ppm. The  $^{13}\text{C}$  NMR spectrum shows only one strong sharp peak for the methoxy carbon at 55.0 ppm and others beyond 100 ppm (the peak at 78 ppm arising from deuterated chloroform)) This indicates that the methoxy group is still present in the polymer and there is no defect in the polymer chain arising from saturated carbons at  $\text{C}_1$  and  $\text{C}_3$  of the isothianaphthene ring.

## 3) UV/Vis. absorption

PMeOITN prepared electrochemically is soluble in many solvents. Figure 3-22 shows its UV/Vis spectrum in dichloromethane. The spectrum of the polymer in the neutral state has an absorption maximum at 393 nm and a strong shoulder at 450 nm. The onset of the absorption band( the  $\pi-\pi^*$



transition band) is at about 700 nm(1.8ev). Thus, the polymer exhibits a band gap of about 1.8ev which is much higher than that of both PDMITN and PITN which are about 1.1ev. The effect of a methoxy group at the 4 position on the band gap of the isothianaphthene polymer can be rationalised on the basis of its steric action. The methoxy substituent is attached to only one side of the isothianaphthene and may induce the adjacent rings to twist, and in turn lower the conjugation.

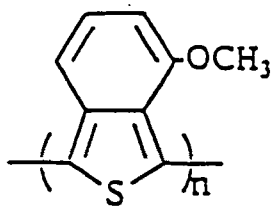
When the polymer was oxidised with trifluoroacetic acid in dichloromethane the absorption shoulder at 450 nm disappeared and two long wavelength peaks at 595 and 760 nm built up. The solution became blue. These features may be due to the formation of radical cations and dications of the polymer. When diethylamine was added to the oxidised polymer solution, the UV/Vis spectrum reverted to that of the original reduced form. This confirms the polymer is optically active and undergoes a reversible chemical redox reaction.

#### **4) X-ray powder diffraction**

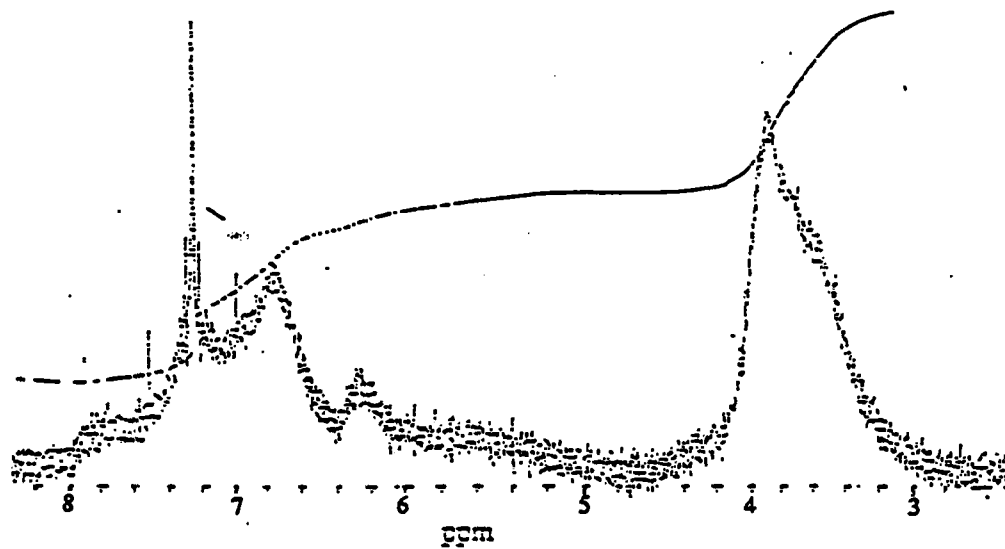
The X-ray powder diffraction pattern of PMeOITN is shown in Figure 3-23. The spectrum shows the polymer to be amorphous. There are only two broad peaks at  $13^{\circ}$  and  $23^{\circ}$ . After doping with iodine the shape of the powder spectrum is the same as that of the undoped polymer although the conductivity of the polymer increases from  $10^{-6}$  to  $10^{-2}$  Scm $^{-1}$ .

#### **5) Gel permeation chromatography**

Since the polymer is soluble in chloroform its molecular weight and molecular weight distribution could be obtained by gel permeation chromatography. The measurement was carried out by the Cookson Technology Centre. The results show that the  $M_n$  and  $M_w$  of the polymer



$^1\text{H}$



$^{13}\text{C}$

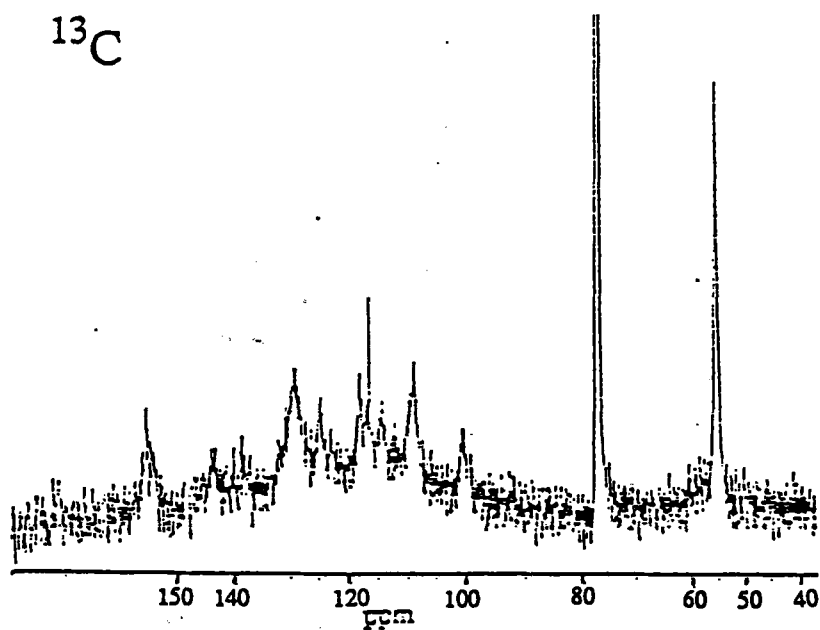


Figure 3-21  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of PMeOITN in deuterated chloroform.

a)  $^1\text{H}$  NMR spectrum and b)  $^{13}\text{C}$  NMR spectrum

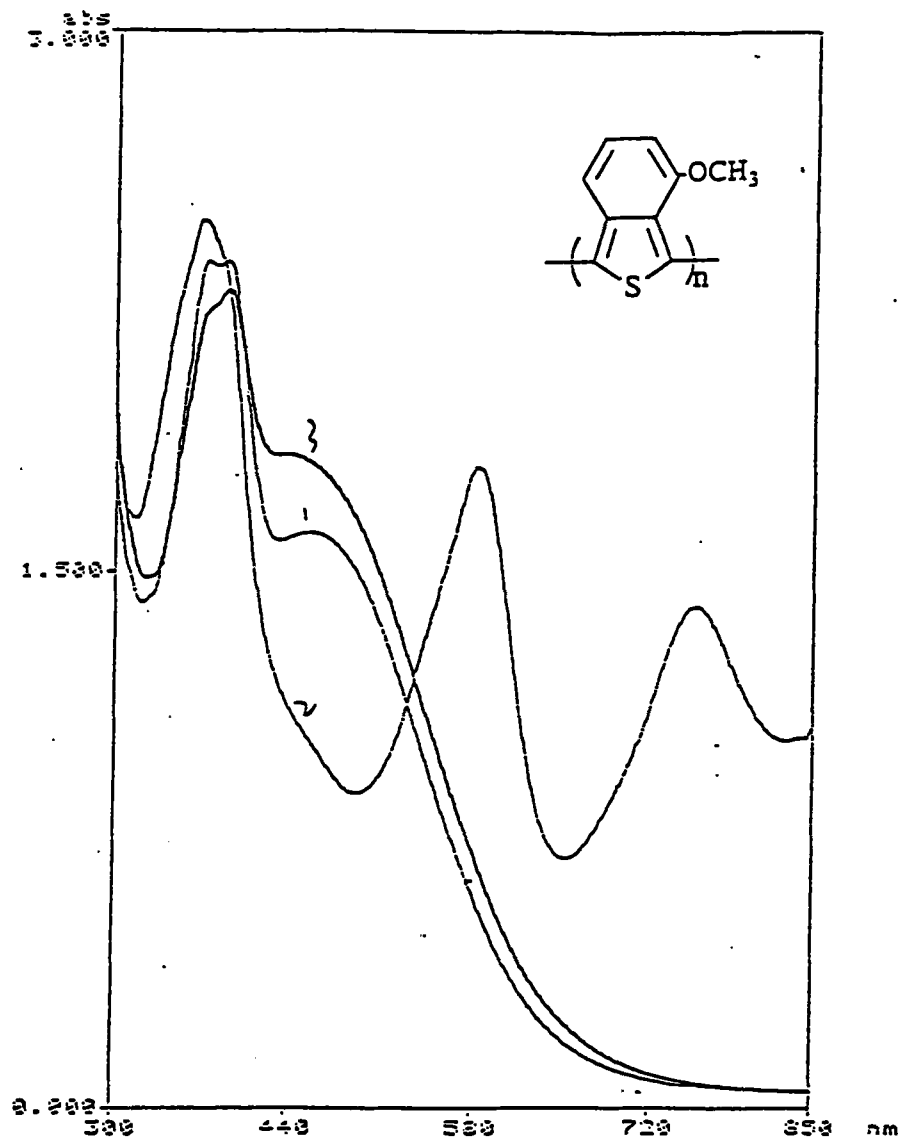


Figure 3-22 UV/Vis. absorption spectra of PMeOITN in dichloromethane. Curve one: directly obtained by electrolysis of MeODHITN, Curve two: doped by trifluoroacetic acid and Curve three: reduced with diethylamine from the doped form.

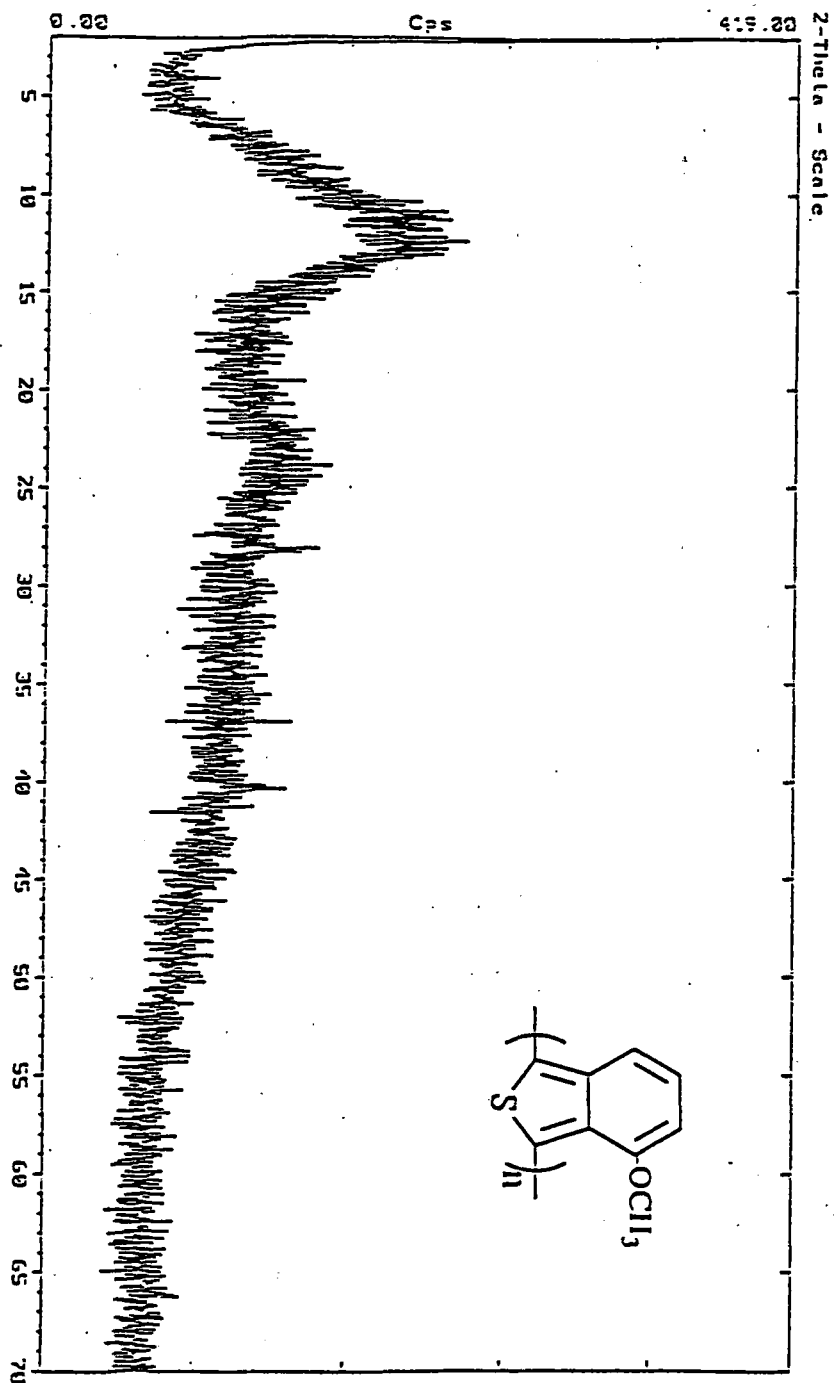


Figure 3-23 X-ray powder diffraction spectrum of PMeOITN made by electrolysis of MeODHITN at 2.0v in the presence of TENBF.

are about 2000 and 3000 Daltons respectively, referenced to a linear polystyrene standard. It seems that the average polymer chain contains 10 to 15 repeat units of the isothianaphthene.

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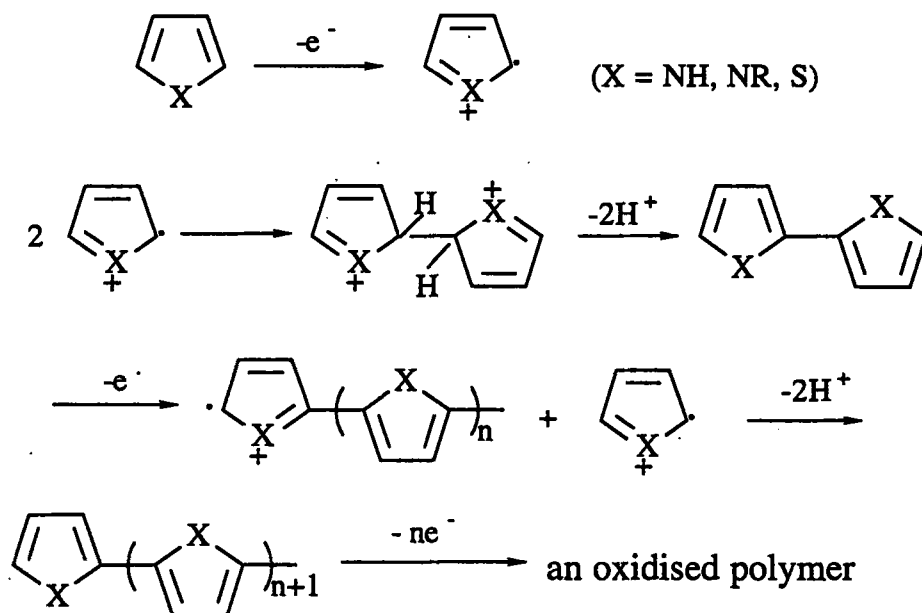


# Chapter Four

## Electrochemical Study of Isothianaphthene Derivatives and Their Corresponding Oxidation Products

### 4.1 Introduction

To understand how the conditions of polymerisation affect the conductivity of the resulting polymers it is important to investigate the reaction mechanism. A widely accepted reaction mechanism is that proposed by Diaz<sup>1</sup> for the electropolymerisation of pyrrole. This is referred to as a radical cation coupling reaction, and is an extension of the ECE reaction mechanism[E(CE)<sub>n</sub>]. The reaction pathway is shown in Scheme 4-1.



Scheme 4-1 Electropolymerisation pathway of heterocyclic compounds

The initial step is the oxidation of the monomer to form a radical cation. These will couple with each other to give a dimer. Deprotonation leads to a conjugated system that can undergo further radical cation formation and coupling to form a conjugated long chain polymer. At the beginning of the

step growth polymerisation only radical cations of the monomer couple to produce dimeric intermediates. However, as the concentration of intermediates on the electrode surface build up a steady-state is set up, which involves the reaction between the monomer, the oligomer and polymeric intermediates<sup>2</sup>. The final stages of the reaction are not clearly understood. Due to the formation of the oxidised conducting product on the working electrode the resulting polymer will incorporate counter anions leading to a polymer-anion composite. This mechanism has also been used to explain the thiophene electropolymerisation process<sup>2</sup>.

Cyclic voltammetry is a very powerful technique to probe the reaction mechanism and redox potentials of components in solution. In this chapter cyclic voltammetry was used to study the electrochemical properties of the isothianaphthene monomers, and their corresponding products, in order to obtain some insight into the reaction mechanism of polymerisation. We examined whether the substituents on ITN affect the oxidation potential and the pathway of the reaction process, and how the reaction conditions (solvents, supporting electrolytes, working electrodes and so on) affect the reaction pathway.

A number of groups have investigated the electro-oxidation behaviour of thiophene monomers during a cyclic potential sweep<sup>4,5</sup>. However, the electro-oxidation of isothianaphthene has not been fully studied by cyclic voltammetry. In all cases mentioned in this chapter the study involved low concentrations of both monomers(0.001M) and electrolytes(0.01M) (unless specifically mentioned).

## **4.2 The Oxidation Potential of Isothianaphthene Derivatives**

Every chemical compound has an oxidation potential. In this section we report the oxidation potentials of a range of isothianaphthenes in acetonitrile

with TENBF as the electrolyte. The initiating oxidation potentials of the monomers recorded by cyclic voltammetry at 100mv/s during the first cycle are given in Table 4-1. In most cases the oxidation peaks of the monomers do not show up in cyclic voltammograms. However, the initiating oxidation potentials could be roughly obtained by examining the potential at which the anodic current started to change sharply (the onset of the anodic current change). The results show that the substituents on the parent ITN do affect the initiating oxidation potential. Electron-donating methyl or methoxy groups result in the oxidation to form the radical cation, taking place at a lower oxidation potential. Interestingly, the fused isothianaphthene derivative, PhITN, showed the highest initiating oxidation potential, at 1.6v. As expected, the 1,3-dihydroisothianaphthene compounds displayed a relatively higher oxidation potential than their fully aromatic counterparts.

Table 4-1 Initiating oxidation potential data of isothianaphthene derivatives(monomers)

| Monomer  | Oxidation potential |
|----------|---------------------|
| ITN      | 1.2v                |
| DHITN    | 1.5v                |
| DMITN    | 1.1v                |
| DHDMITN  | 1.4v                |
| MeOITN   | 1.0v                |
| MeODHITN | 1.3v                |
| PhITN    | 1.6v                |

Note: The initiating oxidation potentials of the monomers(0.001mol) were determined from the onset of the anodic current change in acetonitrile solution with TENBF(0.01mol) at 100 mv/s at the first cycle with a Platinum plate as the working electrode.

All of the voltammograms showed that the monomers underwent irreversible oxidation and that the oxidation current sharply increased after the applied potential reached the point when the monomer started to oxidise. This is in agreement with the irreversible oxidation of the monomer to give radical cations which are very reactive and thus undergo chemical reaction

to form new species. However, unlike the parent thiophene, no polymer film was formed on the working electrode during the potential cycling, when TENBF was used as the supporting electrolyte.

### **4.3 Cyclic voltammetry of DMITN, DMDHITN and Their Polymers**

A good electroactive polymer film with a high conductivity was only formed from DMITN when the electrolyte was TBNBr and dichloromethane was used as the solvent. Under other conditions a black powder with relatively low conductivity was produced. In this section we examine the difference between the voltammograms obtained under a variety of reaction conditions.

#### **4.3.1 Role of the solvent**

##### **1) Acetonitrile**

Comparing Figures 4-1, 4-2 and 4-3 shows that, in the presence of tetraethyl ammonium tetrafluoroborate, varying the solvent does indeed affect the shape of the voltammogram. When acetonitrile was used, besides the oxidation peak of the monomer at about 1.26v (the highest oxidation peak), there were three extra peaks with lower oxidation potentials. The intensity of the oxidation peak of DMITN at 1.26v decreased sharply at first, and then, slowly declined during the subsequent cycling. The peak at ~1.0v had a similar behaviour to the oxidation peak of the monomer. This peak may be attributed to the oxidation of the dimer intermediate. It seems that this intermediate was very quickly formed during the potential cycling. Unlike the peaks at 1.0 and 1.26v, the other two peaks at 0.55 and 0.7v increased progressively and very slowly with the potential sweeping. There

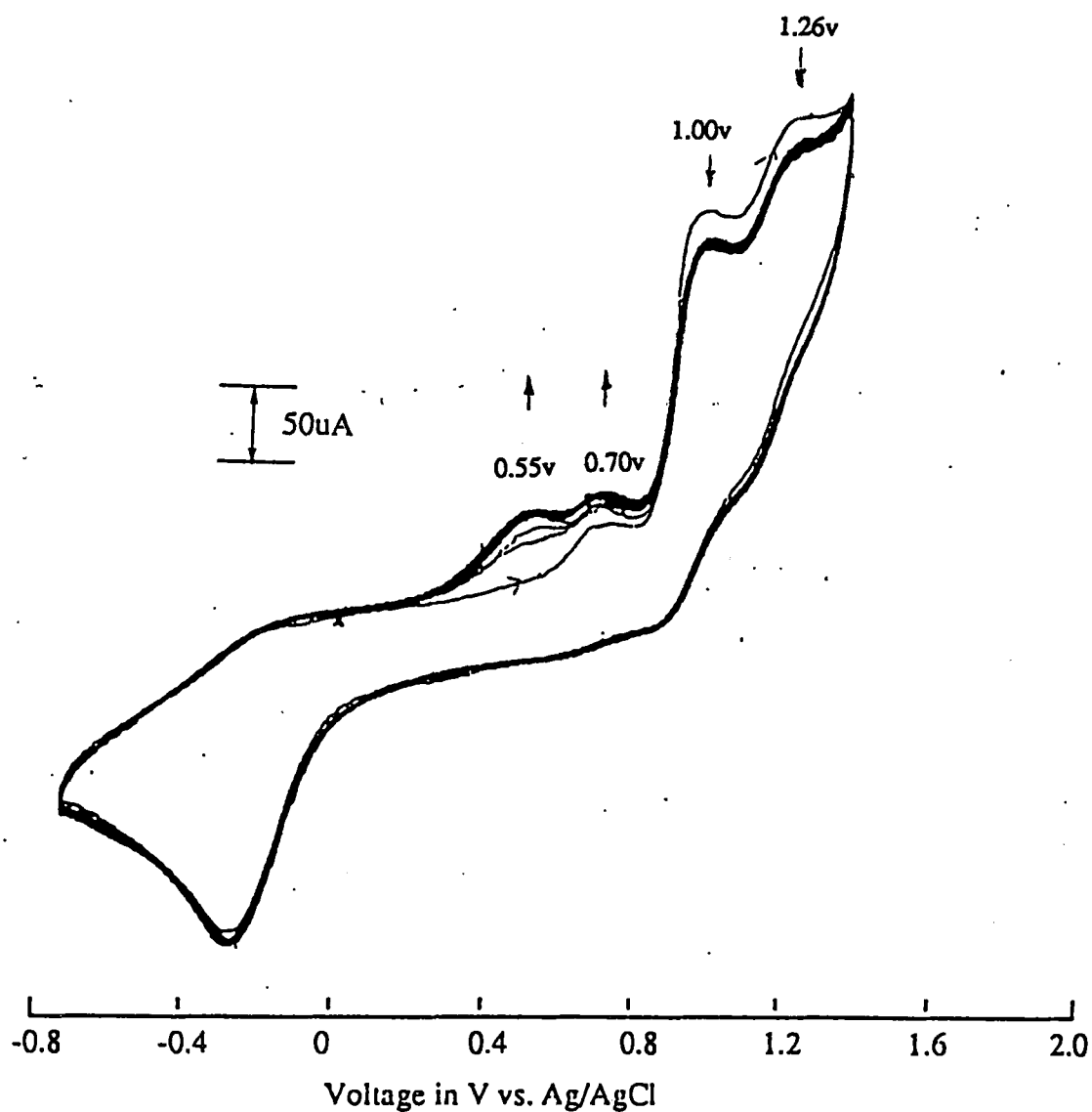


Figure 4-1 Successive cyclic voltammograms of 0.001M DMITN and its oxidation products at a Platinum working electrode in 0.01M TENBF acetonitrile. Scan rate: 100 mv/s (from the second to the tenth cycle).

was only one reduction peak seen at  $\sim -0.3\text{v}$ . It was difficult to assign this peak.

When the potential sweeping was on the positive side, a thin pink coloured film appeared on the surface of the working electrode. As the cycle progressed, the coloured film slowly moved off of the electrode, diffused away and dissolved into the solution. A new film was formed on the electrode on the next cycle. Some green and blue coloured species were also observed on part of the electrode and in the solution after many cycles. However, the pink colour appeared first on the electrode and in the solution. The pink colour lasted for quite a long time at room temperature (several minutes), then eventually, became green and blue after many cycles. This suggests that the pink coloured species is a relatively stable intermediate and not the final polymer product. The polymer film made from ITN is not soluble in most of organic solvents and its colour is blue in the neutral state and transparent in oxidised state<sup>3</sup>. We believe that the pink coloured species is an oxidised intermediate such as a radical cation of an oligomer. This was confirmed by a UV/Vis spectrophotometric study as discussed in the next chapter). Similar oxidised oligomeric thiophenes have been described at room temperature by Garnier and coworkers<sup>6,7</sup>. More recently, Miller, Diaz used ESR and UV/Vis spectrometry to examine the oxidation products of the thiophene oligomers containing between 2 and 6 thiophene units<sup>8,9,10</sup>. These reports confirm that such radical cations are indeed formed in the system and they are relatively stable.

Since the thin pink film diffused from the electrode and dissolved in the solution, further reaction could take place not only on the electrode but also in the solution. Thus, the weak peaks at 0.55 and 0.7v did not significantly build up with cycling. Comparison with the cyclic voltammogram of the polymer product, PDMITN, indicates that these peaks may arise from the

resulting polymer. These results are consistent with the suggestion of Diaz<sup>4</sup> that if the resulting radical cation is very stable it would diffuse away from the electrode surface to form a soluble product. He suggested that only highly reactive radical cations will undergo the radical coupling reaction on the surface of the electrode. If a stable radical cation is formed which diffuses away from the electrode, coupling will only occur in solution and further reaction is only possible if the oligomer so formed diffuses back to the electrode. This may be the reason why no film was formed on the electrode and a deposit was obtained in the solution which had a relatively low conductivity. It seems the stability and activity of the radical cations play a crucial role in the determining the length of the polymer chain and the quality of the polymer film. For example, in the oxidation of the parent thiophene the intermediate radical cation is unstable and extremely reactive. Thus a good polymer film could be formed on the electrode<sup>2,10</sup> even after one cycle.

## **2) Propylene carbonate**

When acetonitrile was replaced by propylene carbonate, the general shape of the cyclic voltammogram was very different, as shown in Figure 4-2a. When the potential was greater than 1.2v the current increased very sharply and rose continuously. The exact position of the irreversible oxidation peak of the monomer was ambiguous. In the second scan a very broad new oxidation peak appeared at a relatively low potential (0.15v) and slowly built up with successive scans. Interestingly, a corresponding reduction peak also built up. After 15 scans the peaks did not increase greatly.

As with acetonitrile, a pink coloured film developed on the electrode, gradually moving off and diffusing into the solution. On a subsequent scan a new pink coloured species would be re-formed on the electrode. When the

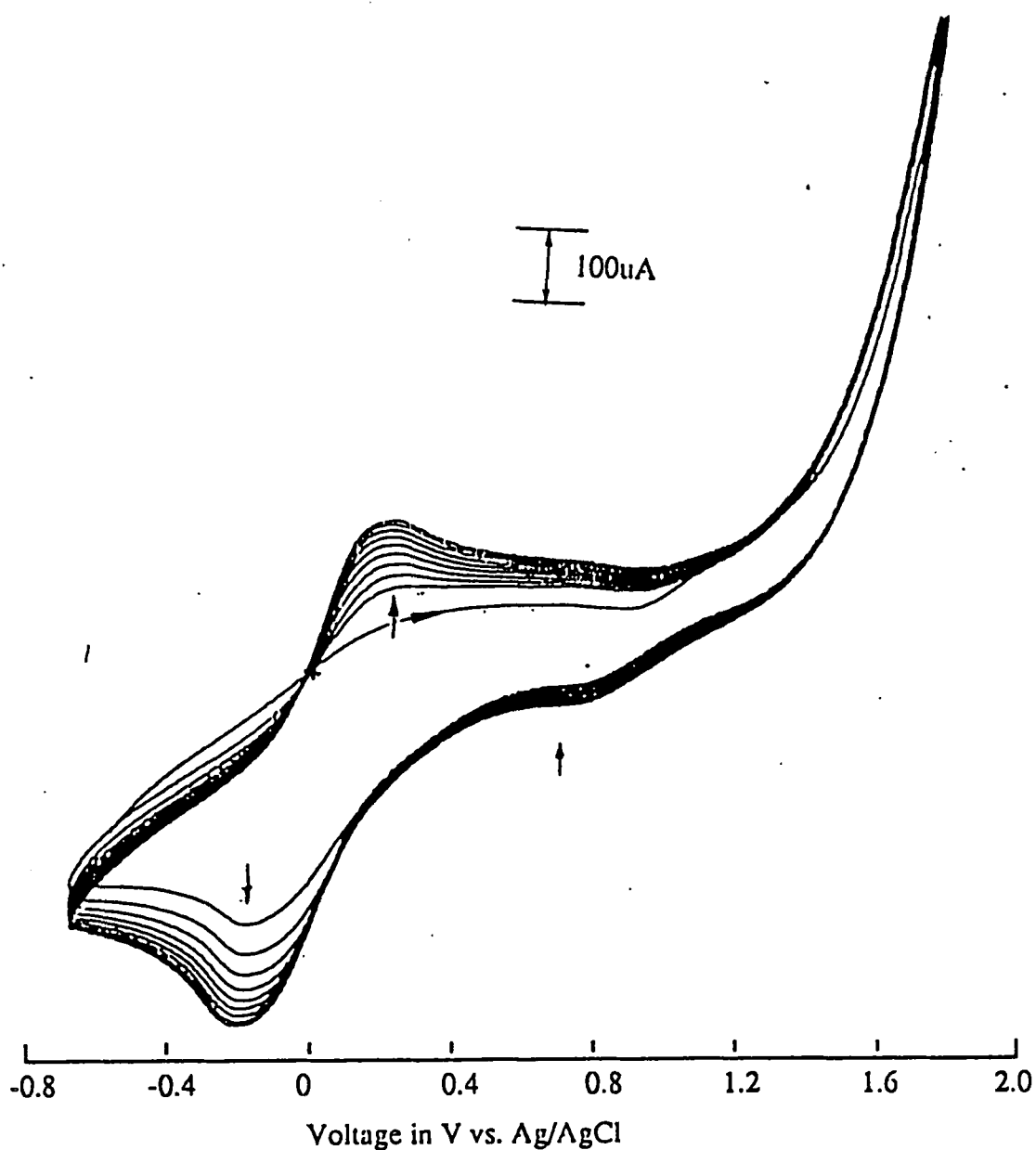


Figure 4-2a Successive cyclic voltammograms of 0.001M DMITN and its oxidation products at a Platinum working electrode in 0.01M TENBF propylene carbonate. Scan rate: 100 mV/s (from the first to the tenth cycle).



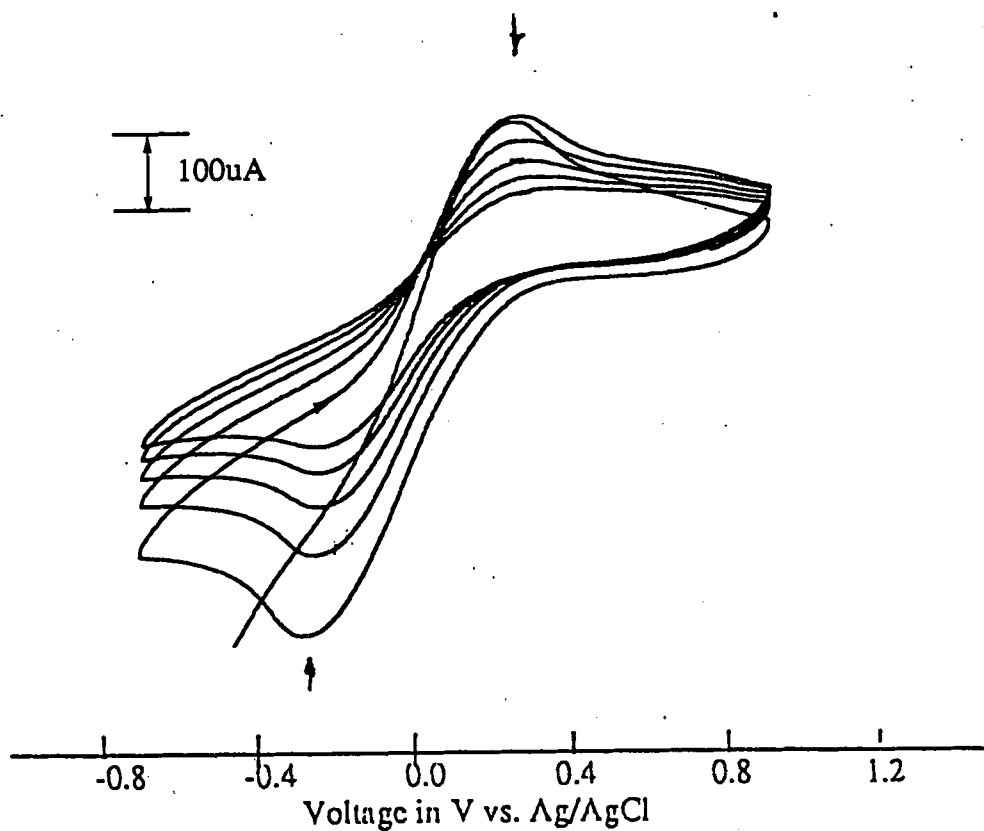


Figure 4-2b Successive cyclic voltammograms of an intermediate which was formed in 0.001M DMITN oxidation in 0.01M TENBF propylene carbonate at a Platinum working electrode after 10 cycles (see Figure 4-2a). Scan rate: 100 mv/s (from -0.7 to 0.9v).

potential was scanned from -0.7 to 0.9v after applying a potential in the range -0.7 to 1.8v, the redox wave in both the oxidation and reduction directions declined and finally disappeared with subsequent cycles (Figure 4-2b). The decline in the redox wave may occur because the thin film of the intermediate species is soluble and does not remain on the electrode. This voltammogram also indicates that when the applied potential is below 1.0v the intermediate species leading to the redox wave is no longer formed.

Whilst there were no oxidation peaks at 0.55 or 0.7v, as in the acetonitrile system, the new redox peaks occurred at an even lower potential (0.15 and -0.2v). This does not result from the oxidation and reduction of the forming DMITN polymer since the polymer is not soluble in propylene carbonate. However, it is not clear what causes this redox wave.

### **3) Dichloromethane**

When dichloromethane was used as the solvent, the cyclic voltammogram (Figure 4-3) was again different. Firstly, the total current during the potential sweep was higher than in the other systems, suggesting a high diffusion rate of the reactive species in dichloromethane. However, the onset of anodic current occurred at a more positive value, at about 1.30v, 0.2v higher than in the acetonitrile system. No other oxidation peak built up. This may also be the result of a relatively high rate of diffusion of the resulting intermediate species from the working electrode into the dichloromethane solution.

Nevertheless, during the potential scan from -0.3v to 1.8v a pink coloured species was formed on the working electrode when the potential was above ~ 1.4v. Formation of the pink coloured species was similar to that in acetonitrile and propylene carbonate. However, the species diffused away more rapidly into the solution. On cycling the solution became pink, then

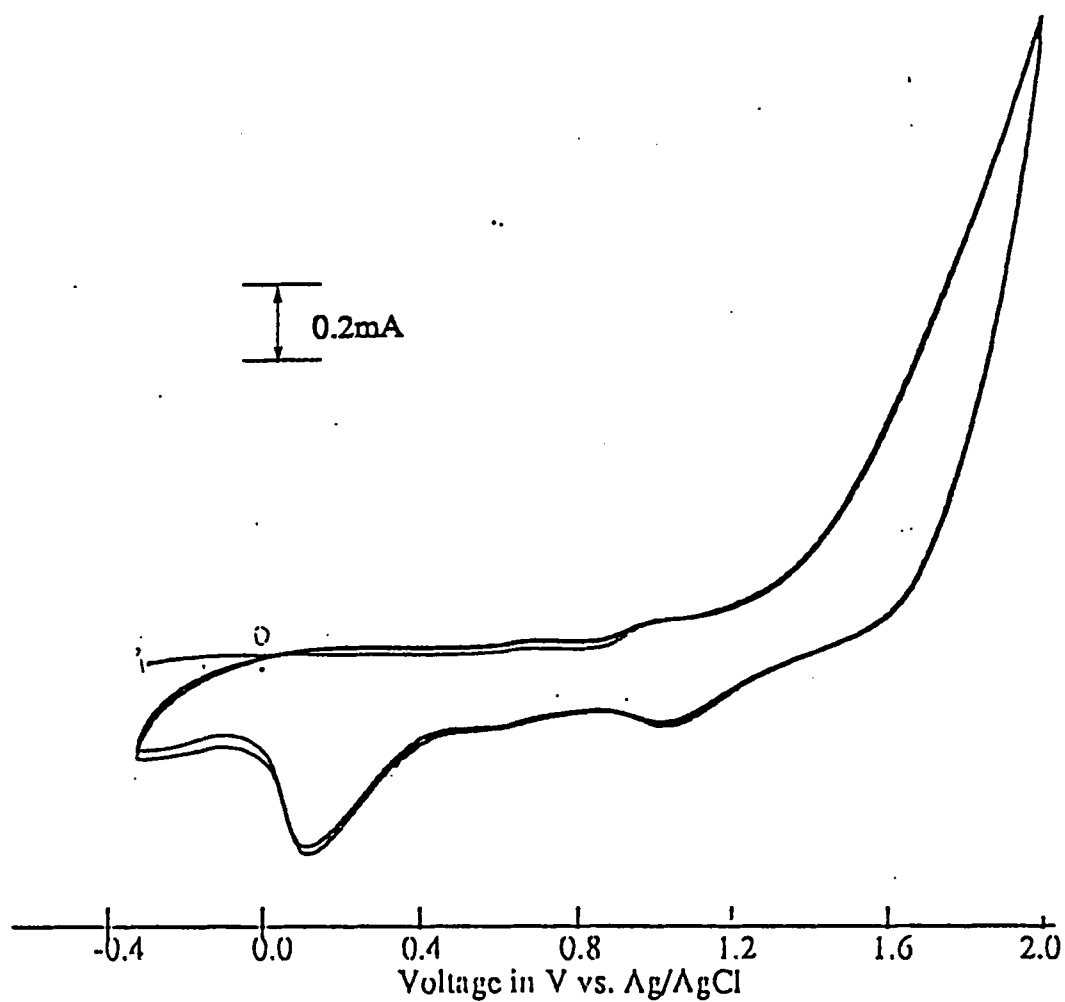


Figure 4-3 Successive cyclic voltammograms of 0.001M DMITN at a Platinum working electrode in 0.01M TENBF dichloromethane. Scan rate: 100 mv/s.

went green and blue. This indicates that more than one intermediate species may be formed in the system and the pink coloured species is further converted to other species. It was found that a precipitate was formed in the solution rather than on the electrode after more than one hour of cycling.

#### **4) Solvent effects on cyclic voltammetry of DHDMITN**

When the 1,3-dihydro compound, DMDHITN, was used in place of the fully aromatic monomer, DMITN, the shape of the cyclic voltammograms was very similar irrespective of solvent (Figure 4-4) and resembled that of DMITN in dichloromethane (Figure 4-3). A strong anodic current was produced when the potential was more positive than 1.4v. The voltammograms did not display a clear initial oxidation peak of the monomer or any other oxidation peak.

In each case, when the potential was scanned to over 1.4v, a pink coloured species was formed on the working electrode which subsequently diffused into the solution. Below this potential nothing could be observed on the electrode. The voltammogram obtained for the potential scanning from -1.0 to 1.4v was similar to that obtained from the background using only the supporting electrolyte in the absence of the monomer.

However, there were some differences between these three solvent systems. Table 4-2 shows that the position of the onset of the anodic current and the unassigned reduction peak in each voltammogram was not the same. The anodic current onset in dichloromethane was more positive than that in acetonitrile and propylene carbonate.

When an ITO was used as the working electrode the shape of the voltammogram of DMDHITN was different. Figure 4-5 shows three oxidation shoulders developing at 0.7, 0.9 and 1.10v. In the second cycle the

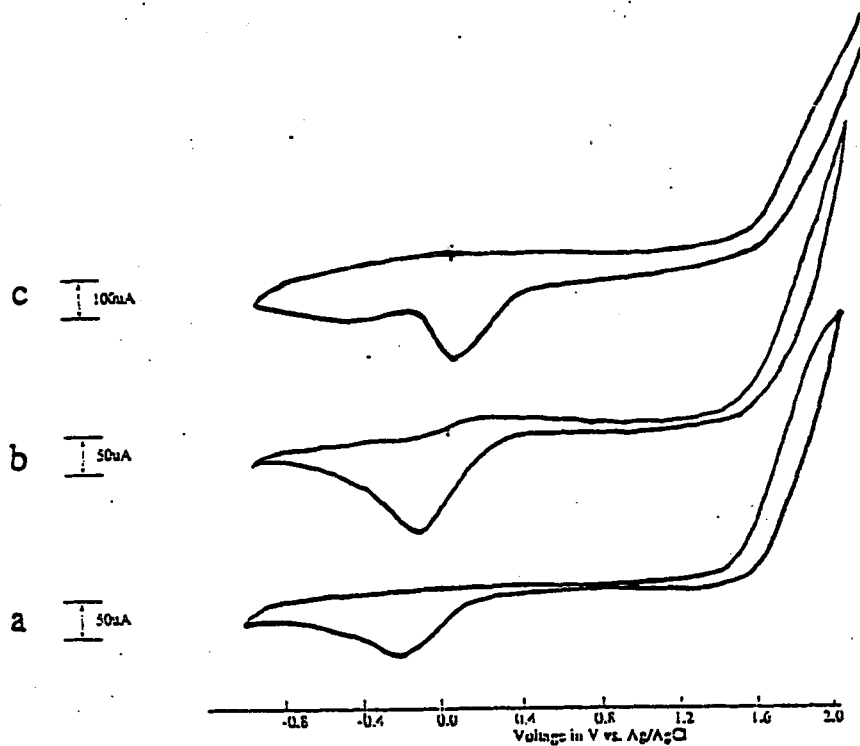


Figure 4-4 Successive cyclic voltammograms of 0.001M DMDHITN at a Platinum working electrode in the presence of 0.01M TENBF (Scan rate: 100 mv/s).

a) in acetonitrile, b) in propylene carbonate and c) in dichloromethane

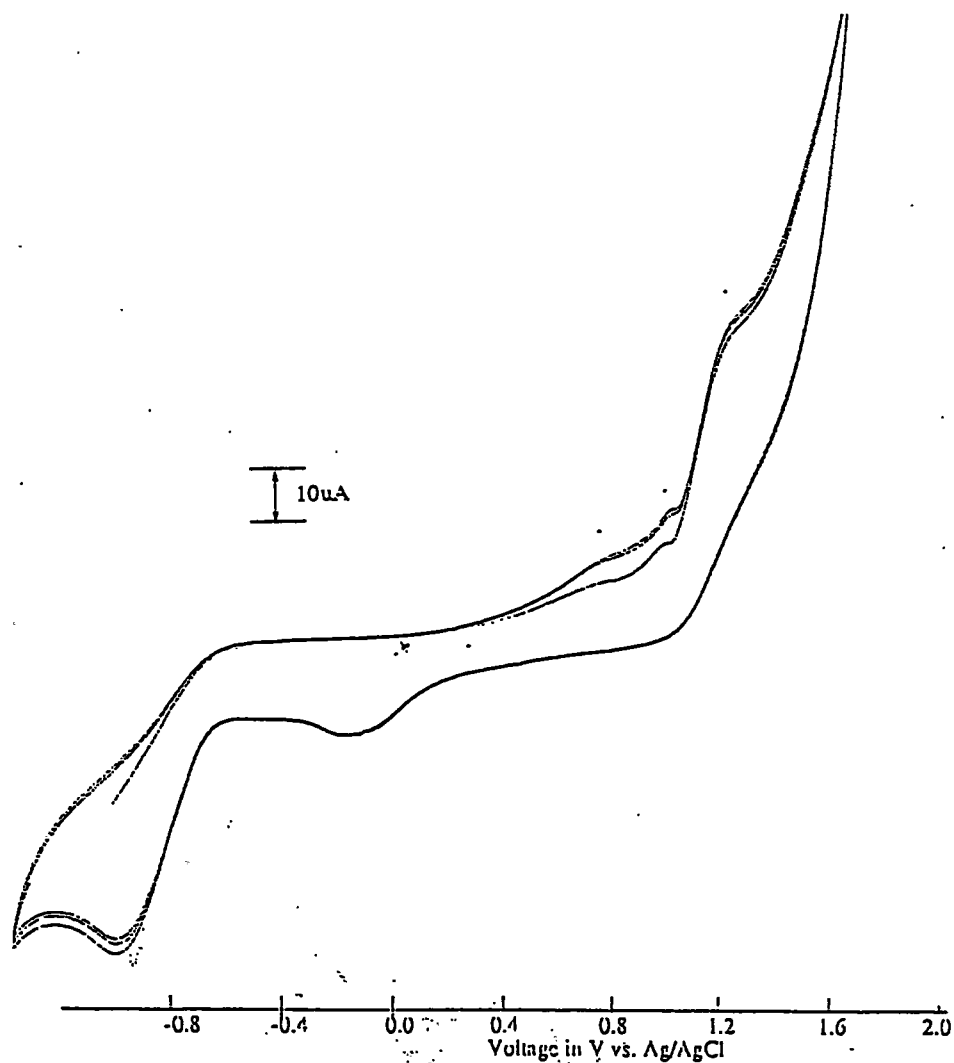


Figure 4-5 Successive cyclic voltammograms of 0.001M DMDHITN at an ITO working electrode in 0.01M TENBF propylene carbonate, from the second to the fourth cycle in 25 mV/s.

oxidation shoulder at 1.10v could clearly be seen. In the following third and fourth cycles the shoulder at 1.10v slightly decreased and two shoulders at 0.7 and 0.9v increased.

Table 4-2 Oxidation and reduction potential data of DHDMITN in a variety of solvents

| Solvent             | $E_a$ | $E_c$ |
|---------------------|-------|-------|
| Acetonitrile        | 1.4v  | -0.2v |
| Propylene carbonate | 1.4v  | -0.1v |
| Dichloromethane     | 1.5v  | +0.1v |

Note:  $E_a$  and  $E_c$  represent the initiating oxidation potential of DHDMITN at the current onset and the unassigned reduction peak, shown in the voltammograms, respectively.

When ITO was used as the electrode the pink colour was not so intense as when platinum was used. The concentration of the pink coloured species may be controlled by the amount of charge passing through the ITO electrode, which was much less than that passing through the Pt electrode at the same applied potential. The anodic current shoulders at 0.7 and 0.9v indicate that some electroactive species do build up on the electrode, which may correspond to the resulting DMITN polymer and oligomer respectively. After 20 cycles a thin blue film was deposited on the ITO electrode. The resulting film, which is insoluble in these three solvents, undergoes reversible electrochemical change.

#### 4.3.2 Role of supporting electrolyte

In the presence of tetraethylammonium tetrafluoroborate (0.01M) a polymer film of DMITN or DHDMITN was not formed on the Platinum working electrode when the concentration of the monomer was 0.001M. In most cases, a pink coloured species diffused away into the solution undergoing further reaction to form a black, less soluble product which was deposited in the solution. In Chapter three we discussed how the type of supporting

electrolyte affected the conductivity of the resulting polymer. Figure 4-6 shows the voltammogram of DMITN obtained using a nucleophilic electrolyte(TBNBr). An extra, strong, reduction peak at 0.35v built up with the potential cycling, and anodic current onset occurred at a very low positive potential (0.5v). However, the oxidation peaks of the monomer and the corresponding product were overshadowed by the oxidation of the supporting electrolyte.

Nevertheless, a green-blue coloured thin film was observed on the platinum electrode when the potential started to be scanned cathodically . This film did not diffuse away, but stuck on the working electrode. Pink coloured species were not observed in this system even on the first potential sweep. After about 20 cycles at 100 mv/s from -0.8 to 1.6v a high quality film was formed on the electrode, even with a dilute concentration of the monomer(0.001M), using dichloromethane as the solvent. The polymer film could also be produced by applying a constant potential in the range of 1.6 to 2.2v for 5 minutes. It seems in the presence of TBNBr both the monomer and the supporting electrolyte were oxidised, the oxidation of TBNBr leading to the formation of the free bromine ( $\text{Br}_2$ )<sup>11</sup>. In the presence of the bromine a highly conducting polyDMITN film was formed. This suggests that the bromine may play a role in the formation of long conjugated polymers. This is unusual, since in most conventional electrochemical studies, it is necessary to avoid reaction with the supporting electrolyte. However, there is some precedence for supporting electrolytes being involved in the radical initiation of polymerisation. Skotheim and coworkers<sup>12</sup> suggested that polymerisation of pyrrole was initiated by a radical produced by oxidation of the supporting electrolyte,  $\text{BF}_4^-$ . This statement was later refuted by several authors <sup>13,14,15</sup>. They favoured the



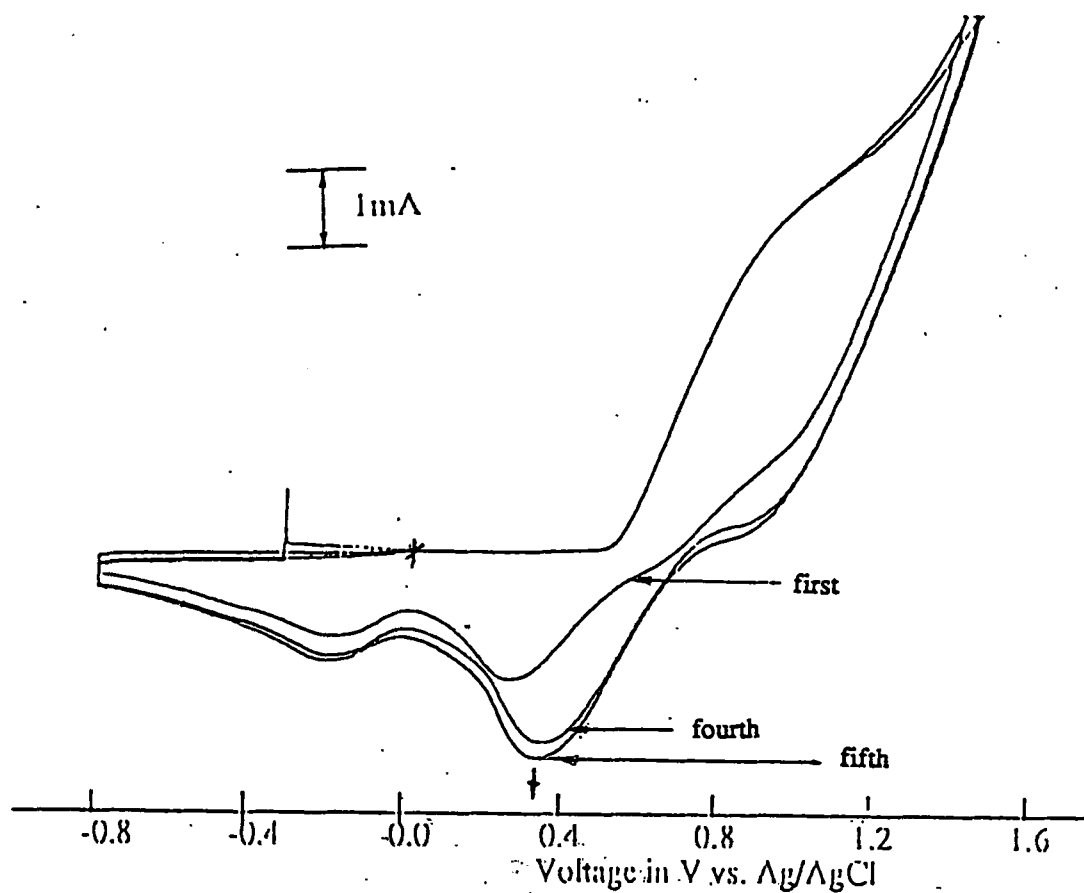


Figure 4-6 Successive cyclic voltammograms for the oxidation of 0.001M DMITN at a Platinum working electrode in 0.01M TBNBr acetonitrile, from the first to the fifth cycle in 50 mv/s.

initiation of the monomer by electron loss on the working electrode to produce a radical cation, followed by radical coupling. They found that the rate of polymer growth was not limited by diffusion of the pyrrole to the electrode, but, was controlled by the formation of the radical cation. The present work agrees with the rate-limiting step being the radical cation coupling. Thus, we do not agree with the suggestion that initiation of the monomer occurs by the oxidation of the supporting electrolyte. If this were the case the formation of the polymer would take place throughout the solution rather than just on the surface of the working electrode.

Under the same condition the 1,3-dihydro monomer, DMDHITN, (0.001M) did not form a polymer when TBNBr(0.01M) was used as the supporting electrolyte in acetonitrile or dichloromethane. The voltammogram of the monomer was the same as that of TBNBr. This is very surprising, since in the presence of a high concentration of the monomer(>0.1M) and electrolyte(>0.2M) a highly conducting polymer was obtained. An explanation of this feature has not been found.

#### **4.3.3 Cyclic voltammograms of poly(5,6-dimethylisothianaphthene)**

In this section we discuss the voltammograms of the polymer films prepared from DMITN under different conditions. Figures 4-7 and 8 show typical cyclic voltammograms of films of poly(5,6-dimethylisothianaphthene) previously grown on an ITO coated glass and Platinum electrode respectively{in dichloromethane with TBNBr (0.01M), DMITN(0.001M)}. The film deposited on the ITO had two oxidation peaks at 0.30 and 0.75v and two reduction peaks at 0.15 and 0.65v respectively. The film produced on the Platinum plate exhibited one oxidation peak with one shoulder at almost the same positions as those in the ITO system. However, the

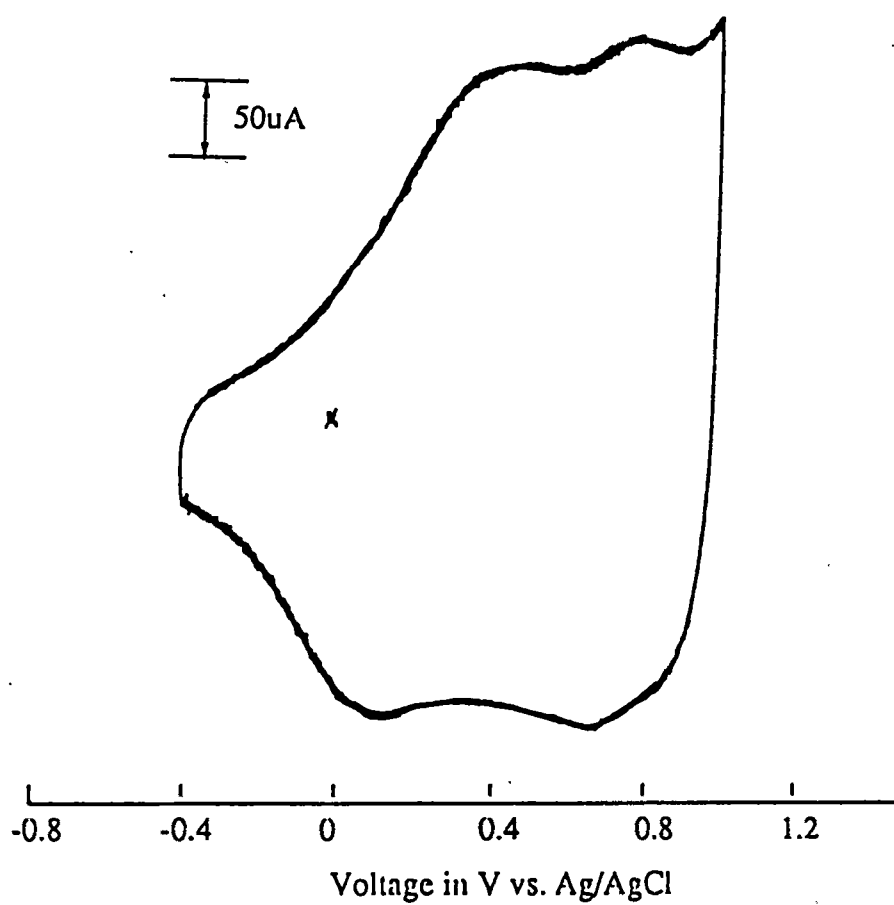


Figure 4-7 Successive cyclic voltammograms of PDMITN formed on an ITO working electrode in 0.01M TENBF acetonitrile. Scan rate: 50 mv/s.

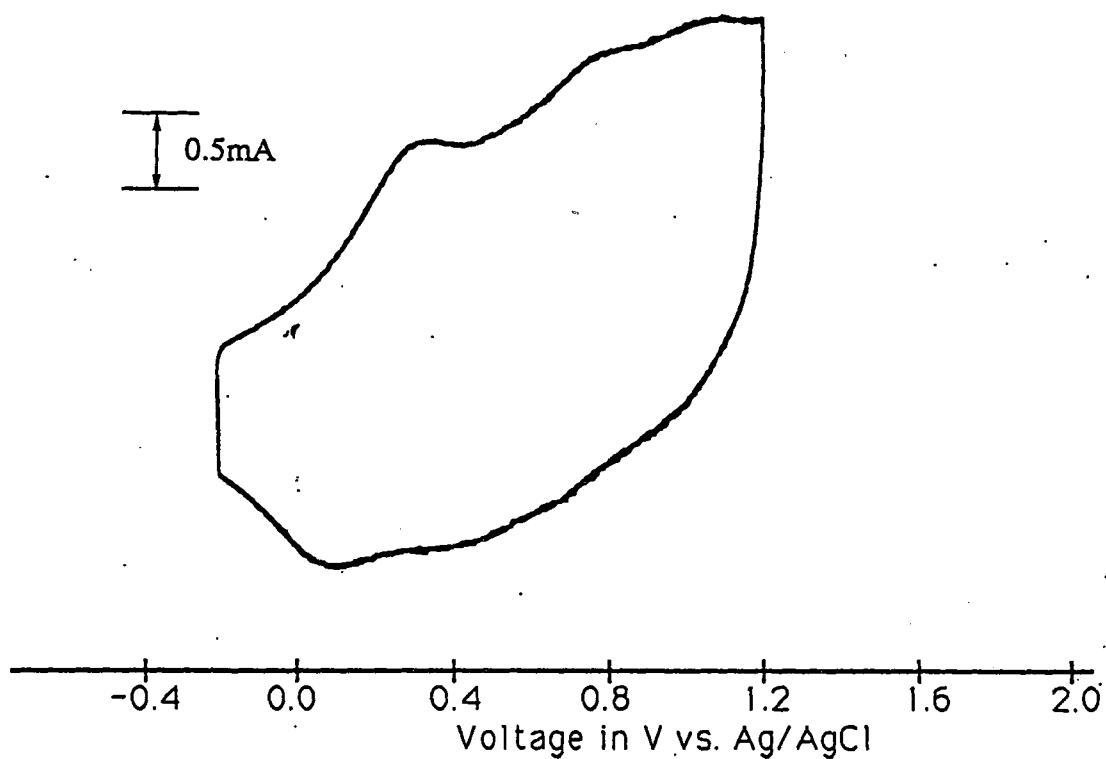


Figure 4-8 Successive cyclic voltammograms of PDMITN formed on a Platinum working electrode in 0.01M TENBF acetonitrile. Scan rate: 50 mv/s.

reduction peaks are slightly different, at 0.10v with a shoulder at about 0.50v. The shape of the voltammograms is unchanged with potential cycling. Cycling of both films could be repeated between the oxidised and neutral states in a range from -0.4 to 1.2v with no appreciable decomposition of the material. On cycling an associated high contrast colour change occurred from blue in the neutral form to yellow/transparent in the oxidised form. This behaviour is similar to that of the polymer film prepared from the parent isothianaphthene<sup>17</sup>. This indicates that the introduction of two methyl groups at positions 5 and 6 of the ITN ring does not significantly affect the energy gap of the ITN polymer. This result confirms the suggestion made by Bredas et al<sup>16</sup> using valence effective Hamiltonian band-structure calculations.

However, there is a significant difference between the voltammograms of PDMITN produced in our work and that of PITN reported by Kobayashi et al<sup>17</sup>. PITN was reported to show only one stable oxidation peak at ~ 0.6v and one reduction peak at ~ 0v. They also mentioned that when the scan range was set from -0.3 to 1.3v another unstable redox peak was observed at 1.1v(oxidation) and 0.5v(reduction). The polymer also started to degrade. In the PDMITN system only when the scan range was increased to over 1.4v did the corresponding anodic current sharply rise and the PDMITN film become permanently black. On the second cycle the current was greatly diminished. It was noted that the black film had broken away from the electrode. This indicates that the electron donating methyl groups enhance the oxidation stability of the polymer film compared with the ITN polymer.

The presence of two stable redox peaks (very broad) in the PDMITN system is intriguing. The low redox peaks could belong to the polymer and the oligomers or short chain DMITN polymers may give rise to the redox peaks at a relatively high potential(0.75v for oxidation and 0.65v for reduction).

A second suggestion is that the oxidation of PDMITN film takes place in two steps, first the polymer is converted to the radical cation by a one electron loss and then further oxidised to the dication form by a second electron loss, obeying the one electron transfer mechanism. This suggestion would need to be confirmed by in situ-ESR examination.

The kinetics and reversibility of the charge-discharge cycle were also explored using the potential scan-rate,  $v$ , as a variable parameter.

Representative data are shown in Figures 4-9 and 4-10 ( the polymer film was made under the same conditions as that shown in Figure 4-8). The direct proportionality of the peak current with  $v$  (instead of  $v^{1/2}$ ) confirms the surface-confined nature of the species responsible for the redox process in PDMITN. The cyclic voltammograms of the polymer film were kinetically reversible over a sweep rate change from 20 to 80mv/s. The position of the oxidation and reduction peaks was almost unchanged.

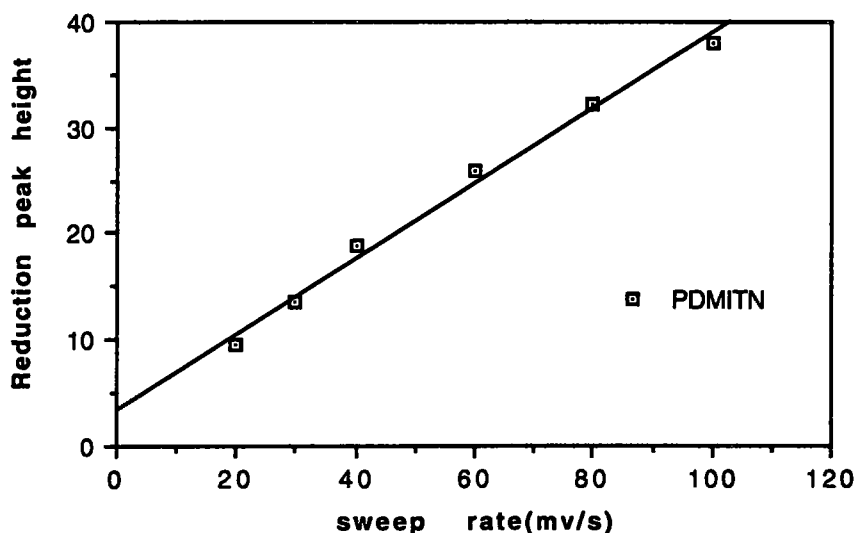


Figure 4-10 Dependence of the cathodic peak current on potential scan rate for a PDMITN film

To prepare a polymer film on the electrode from the 1,3-dihydro monomer, DMDHITN, high concentrations of both the monomer(0.2M) and

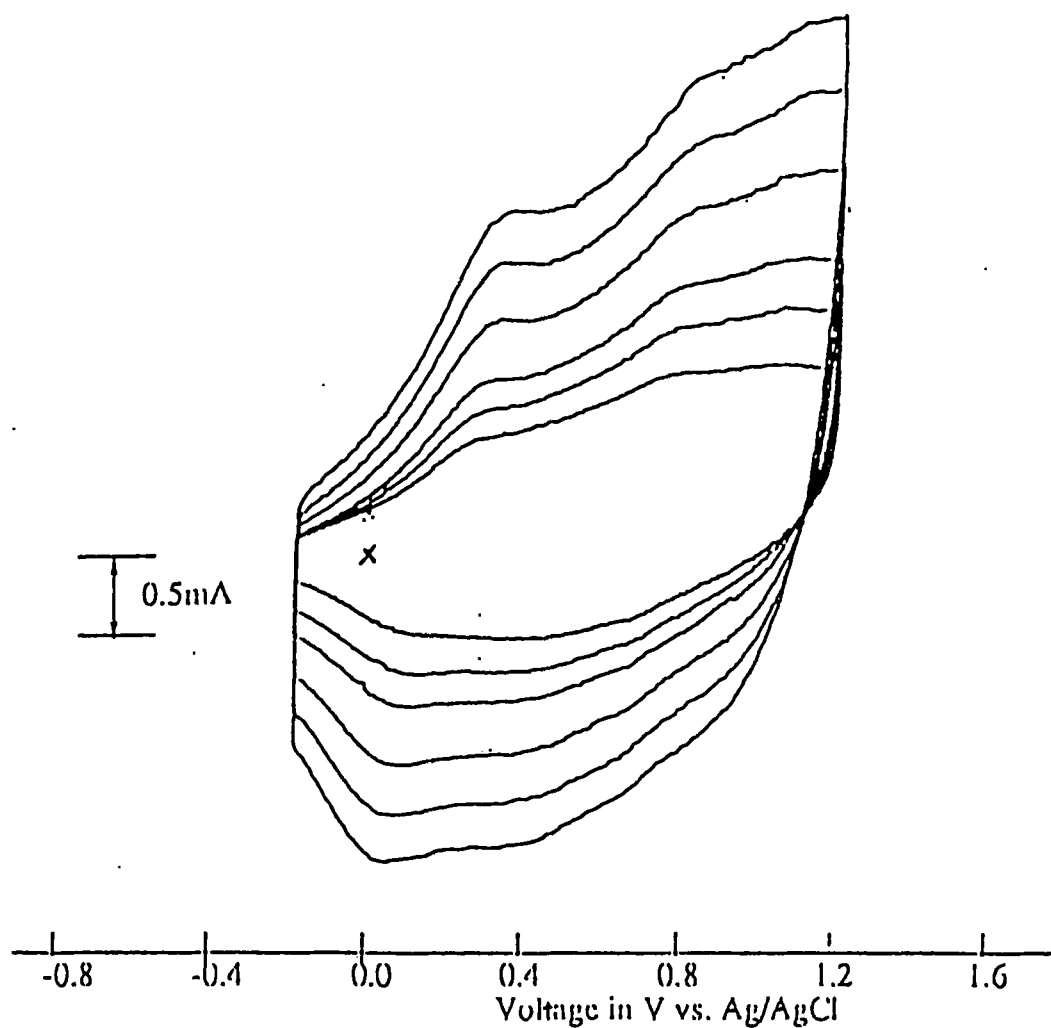


Figure 4-9 Cyclic voltammograms of PDMITN at different scan rates of 20, 30, 40, 60, 80 and 100 mV/s respectively, on a Platinum working electrode in 0.01M TENBF acetonitrile.

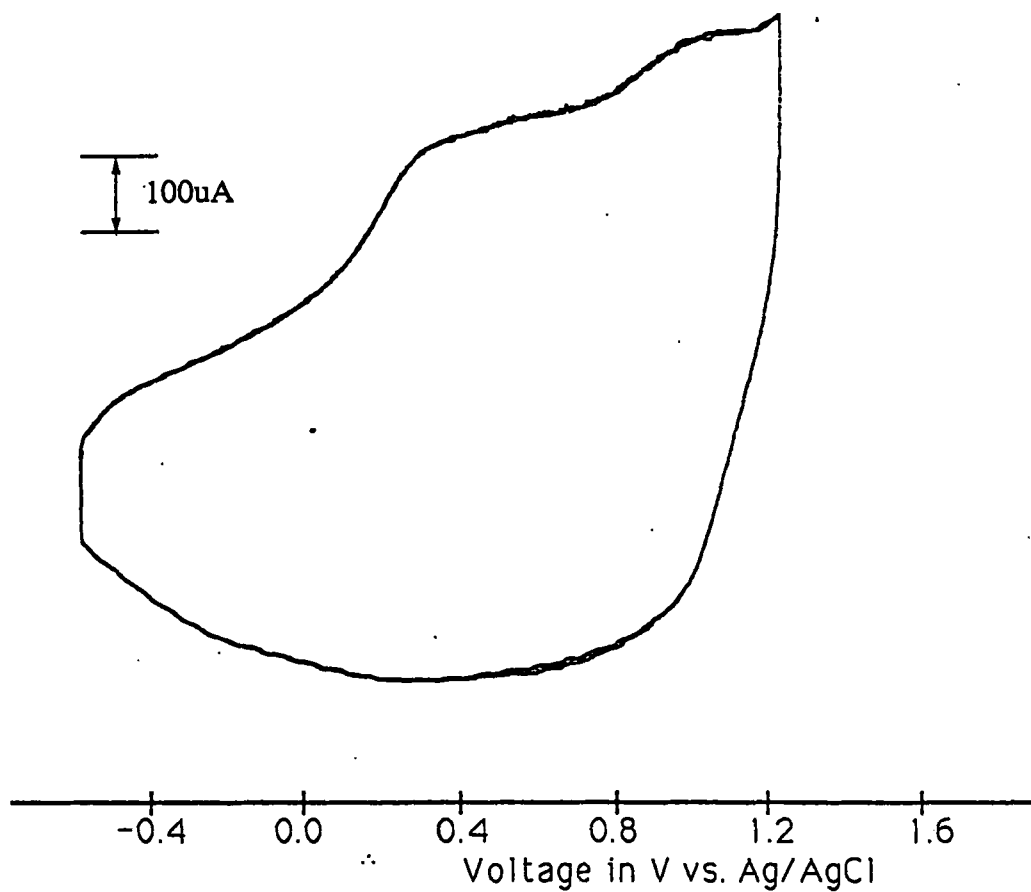


Figure 4-11 Successive cyclic voltammograms of PDMITN formed from DMDHITN on a Platinum working electrode in 0.01M TENBF acetonitrile. Scan rate: 60 mV/s.



the supporting electrolyte(0.2M) were essential. Figure 4-11 shows the voltammogram of the polymer film so obtained. The cyclic voltammogram was similar to that of the film made from DMITN. The colour of the film changed from blue(neutral state) to slightly yellow-transparent(oxidised state). There was one oxidation peak at 0.3v and one shoulder at ~0.80v. The potential cycling process was reversible. The shape of the cyclic voltammogram was unchanged after more than 500 cycles provided that the potential sweep was not over 1.4v. This indicates that the film made from DHDMITN undergoes resversible redox reaction and has a very good stability.

We tried to produce a free standing thick film, by electropolymerisation at a series of monomer and electrolyte concentrations using a range of constant potentials from 1.5 to 2.4v in dichloromethane. However we failed to obtain a free standing film. Instead, owing to the fragility of the resulting polymer film, a black powder was deposited on the electrode and in solution.

#### **4.4 Cyclic Voltammetry of ITN, DHITN and their Polymers**

Since polyisothianaphthene was first reported by Wudl and coworkers in 1984 several reports have been published on the electrochemistry of this polymer. However, there have been no reports on an electrochemical study of the ITN monomer and no cyclic voltammograms of the monomer solution has been published. In this section cyclic voltammetry of ITN and DHITN are discussed

##### **4.4.1 Role of solvent**

###### **1) Effect on ITN**

Figure 4-12 shows the voltammogram of ITN(0.001M) using a Platinum plate in acetonitrile with TENBF(0.01M) as the supporting electrolyte. In

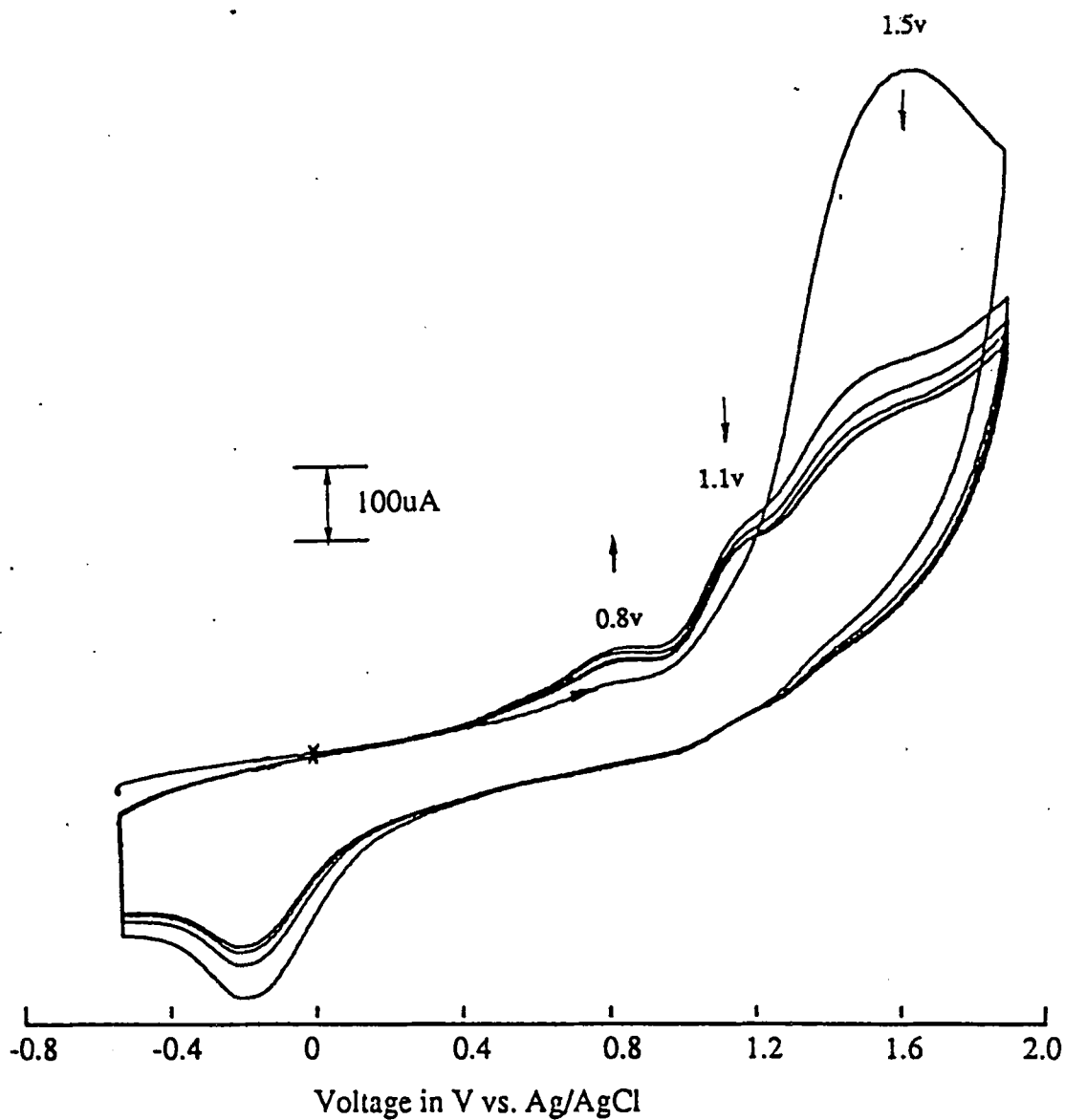


Figure 4-12 Successive cyclic voltammograms of 0.001M ITN and its oxidation products at a Platinum working electrode in 0.01M TENBF acetonitrile. Scan rate: 25 mv/s (from the first to the fifth cycle).

the first cycle the onset of the anodic current started at about 1.2v. Further sweeping above 1.2v caused the current to sharply increase and reach a peak at ~1.5v. During the following cycle the oxidation peak at ~1.5v dropped dramatically giving two shoulders at ~1.1 and ~1.4v. The two shoulders slowly declined over the next four cycles, to a steady-state value. At the same time a new oxidation peak at a low potential (0.80v) built up very slowly. The anodic current in the range from 0.3 to 0.9v increased gradually with the cycling. The oxidation peak at 1.5v may result from the oxidation of the ITN monomer. The current decay of the oxidation peak indicates that the ITN monomer electrooxidises irreversibly. But, the irreversible shoulder at 1.1v is very difficult to assign. This may be the irreversible oxidation of an intermediate from ITN. The increase in the anodic current between 0.3 and 0.90v during the potential sweep clearly indicates the formation of an electroactive species on the working electrode. This is contrary to the suggestion of Wudl<sup>3</sup> that an electro inactive poly(1,3-dihydroisothianaphthene) is formed when a non-nucleophilic electrolyte such as TENBF or TBNPF is used. If this is the case the working electrode would be covered with the polymer and the anodic current should decrease.

As with DMITN, a pink coloured species was formed on the electrode, which diffused away slowly. The pink coloured species was subsequently converted to a green-blue coloured species in the solution or at the electrode. Finally, a black precipitate was observed in the solution. This indicates that the monomer could be converted into a relatively stable intermediate which undergoes further reaction in solution to produce the polymer as a precipitate. Therefore, in the voltammograms of DMITN and ITN any oxidation peak associated with the polymer will be very weak. In contrast, the oxidation peak of the intermediate will show up much more strongly.

When propylene carbonate was used as the solvent the shape of the cyclic voltammogram (Figure 4-13) was similar to that of DMITN under the same conditions. However, the redox peaks were more separated, 0.30v (oxidation) and -0.50v(reduction) giving a redox wave ( $E_{1/2}$ ) of 0.80v, compared with 0.40v for DMITN.

When the solvent was changed to dichloromethane the features exhibited in acetonitrile and propylene carbonate disappeared. There were no extra oxidation peaks, except the residual current peak corresponding to the oxidation of the monomer. Nevertheless, in common with the other solvents the pink coloured species was formed on the electrode which diffused away with subsequent cycles. In dichloromethane the diffusion of the pink coloured species was so fast that the whole solution rapidly became pink.

## 2) Effect on DHITN

Jen<sup>18</sup> and Gumbs<sup>19</sup> have already reported that DHITN could be converted into PITN even although DHITN is not a 'fully aromatic' compound. In Chapter three NMR, FTIR and elemental analysis showed that the polymer made from DHITN was identical to the polymer made from ITN. However, the cyclic voltammograms of DHITN(Figure 4-14) exhibited a very simple pattern in the three solvent systems, similar to the behaviour of DMDHITN. On the anodic sweep with a Platinum electrode, no significant electroactivity was observed, apart from the residual current peak corresponding to the oxidation of the monomer. On cathodic sweep, a clear reduction peak below 0.1v was observed which slightly increased with cycling to a steady-state value.

The voltammograms of DHITN in propylene carbonate using an ITO electrode are shown in Figure 4-15. Our results are consistent with those

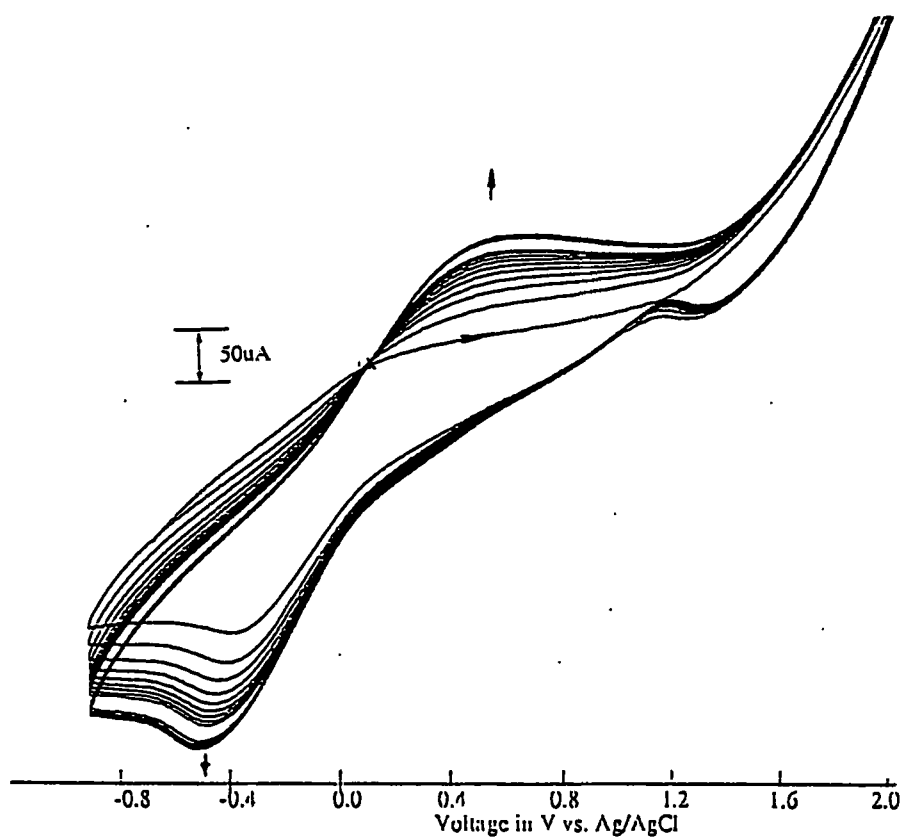


Figure 4-13 Successive cyclic voltammograms of 0.001M ITN and its oxidation products at a Platinum working electrode in 0.01M TENBF propylene carbonate. Scan rate: 25 mv/s (from the first to the twentieth cycle).

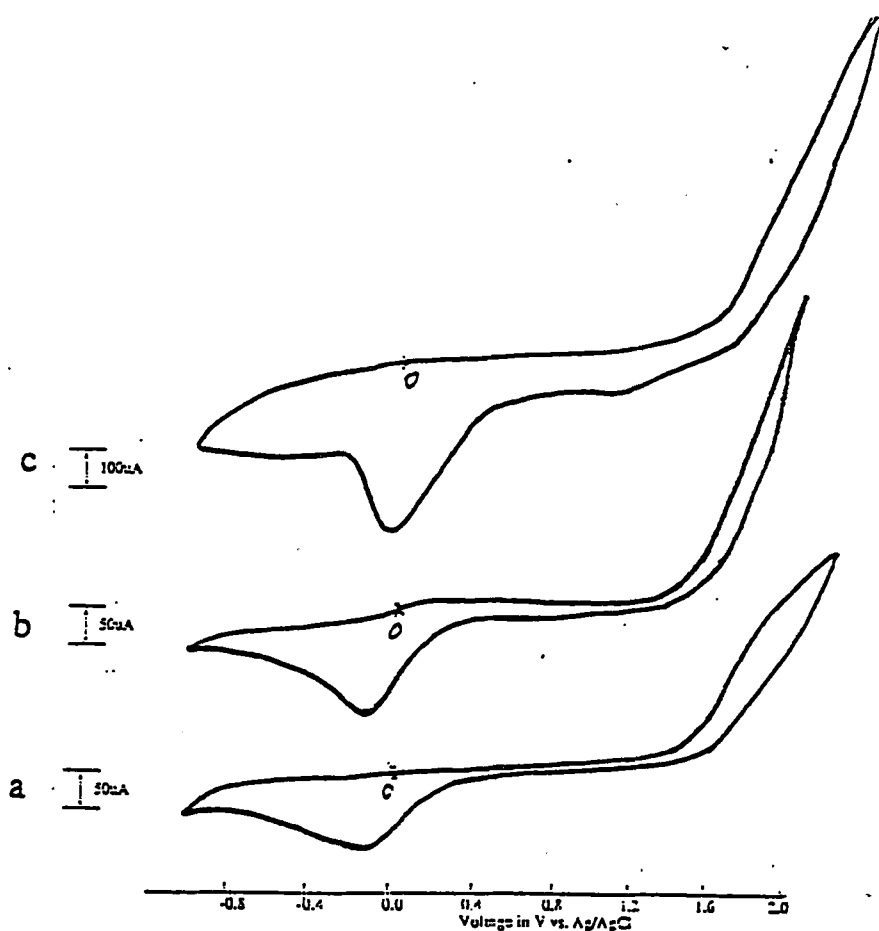


Figure 4-14 Successive cyclic voltammograms of 0.001M DHITN at a Platinum working electrode in the presence of 0.01M TENBF (Scan rate: 100 mv/s).

a) in acetonitrile, b) in propylene carbonate and c) in dichloromethane

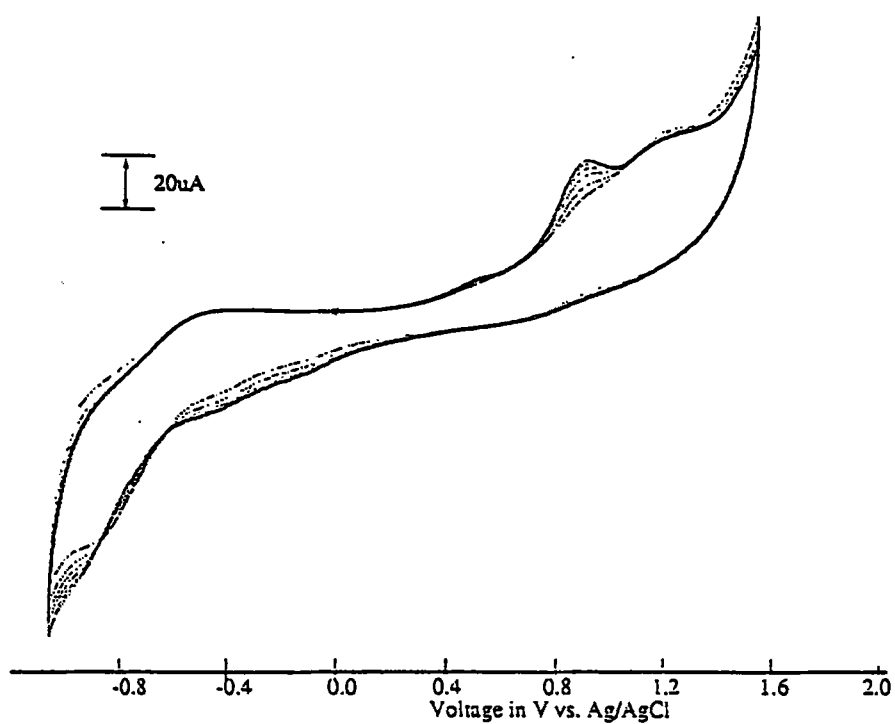


Figure 4-15 Successive cyclic voltammograms for the oxidation of 0.001M DHITN at an ITO working electrode in 0.01M TENBF propylene carbonate. Scan rate: 50 mv/s from the first to the the sixth cycle.

described in ref. 17. Besides a large catalytic current, resulting from the oxidation of the monomer, a very small oxidation peak at 0.55v was observed, and the corresponding cathodic current below -0.70v was sharper and stronger. Two extra small oxidation peaks at 0.90 and 1.30v were clearly visible with potential sweeping. The peak at 0.90v increased progressively with sweeping. The reduction peaks increased as well. The oxidation peak at 0.55v was assumed to result from oxidation of the polymer (see the voltammograms of the ITN polymer in Figure 4-17). The peaks at 0.90 and 1.30v could be attributed to intermediates formed during the irreversible monomer oxidation. This indicates that use of an ITO electrode leads to a series of relatively stable intermediates which could be absorbed on the ITO electrode. The pink coloured species could still be seen diffusing away from the electrode. After the cell was dismantled, a very thin blue film was observed on the electrode, which is electroactive. The film was not found when a Platinum plate was used as the electrode under the same conditions. This may give a clue as to why the conductivity of the polymer made using an ITO electrode is higher than that of the polymers made using a Platinum electrode.

#### **4.4.2 Effect of supporting electrolyte**

When a nucleophilic electrolyte (TBNBr) was used a blue film was formed on the Platinum electrode even in very dilute solutions of the ITN monomer (0.001M). As with DMITN in the presence of TBNBr, although the oxidation peak of the polymer film could not be identified owing to the strong anodic current caused by oxidation of the electrolyte, the reduction peak of the polymer film was clearly visible(Figure 4-16). On further cycling the reduction peak at 0.35v increased progressively and the position of the peak shifted slightly owing to the growth of the polymer film on the electrode giving rise to IR(voltage) drop (I is current and R is resistance).



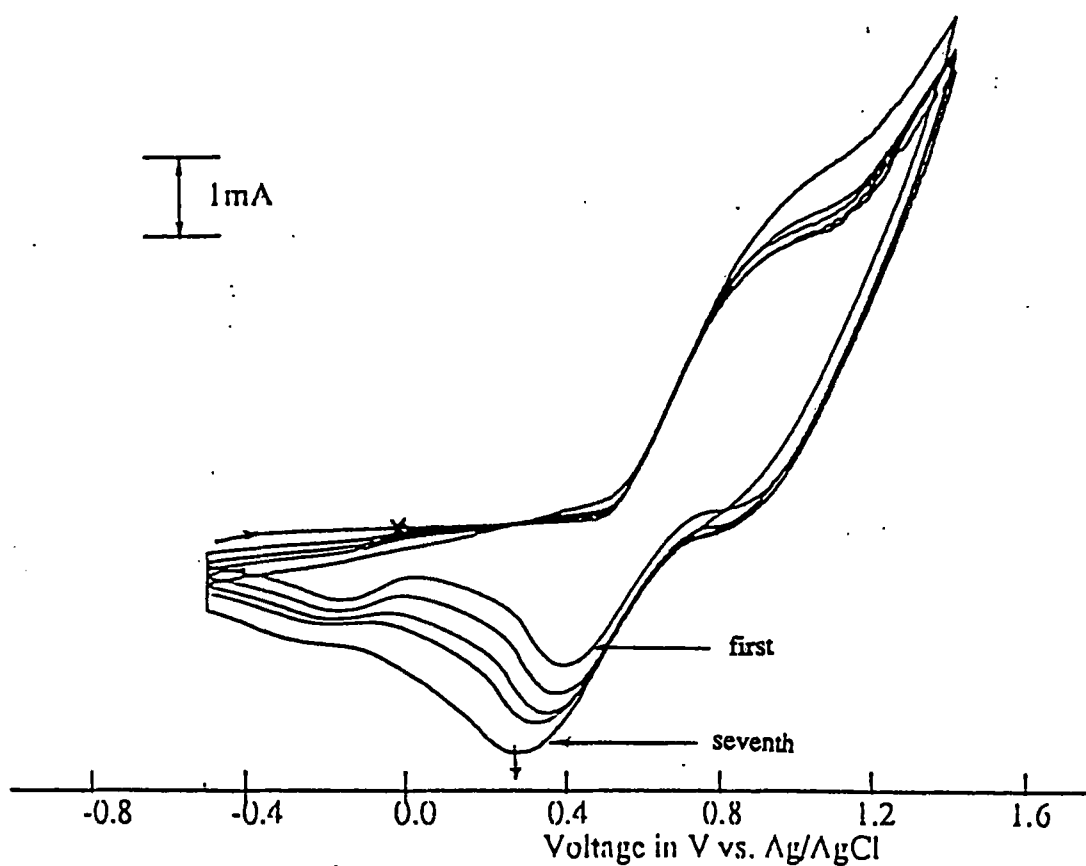


Figure 4-16 Successive cyclic voltammograms for the oxidation of 0.001M ITN at a Platinum working electrode in 0.01M TBNBr acetonitrile, from the first to the seventh cycle in 50 mv/s.

After 5 minute of cycling a bright blue electroactive film was obtained on the electrode.

Under the same conditions the 1,3-dihydro monomer, DHITN, (0.001M) did not form a polymer when TBNBr(0.01M) was used as the supporting electrolyte in acetonitrile or dichloromethane. The voltammogram of the monomer was the same as that of TBNBr. This is very surprising, since in the presence of a high concentration of the monomer(>0.1M) and the electrolyte(>0.2M) in acetonitrile a highly conducting polymer was obtained. An explanation of this feature has not been found.

#### **4.4.3 Cyclic voltammograms of polyisothianaphthene**

##### **1) Polymers formed from ITN**

A number of papers have discussed the cyclic voltammogram of polyisothianaphthene<sup>17,20</sup>. However the cyclic voltammograms are somewhat ambiguous. In reference 20 the redox peak is not well defined and the redox wave seems broad. The corresponding oxidation and reduction peaks are located at the relatively high potential of 0.80 and 0.70v respectively. It seems that the film produced in the published work may be a mixture of the polymer and oligomer.

In this work a high quality polyisothianaphthene film was produced on a Platinum electrode by potential switching from -0.6 to 1.6v for 5 minutes in dichloromethane with 0.001M of ITN and 0.01M of TBNBr. The cyclic voltammogram of the polymer film is shown in Figure 4-17. The redox peaks were well defined. The redox wave was 0.30v, corresponds to an oxidation peak at 0.50v and a reduction peak at 0.20v. This wave is much more narrow than that of poly(5,6-dimethylisothianaphthene) which was

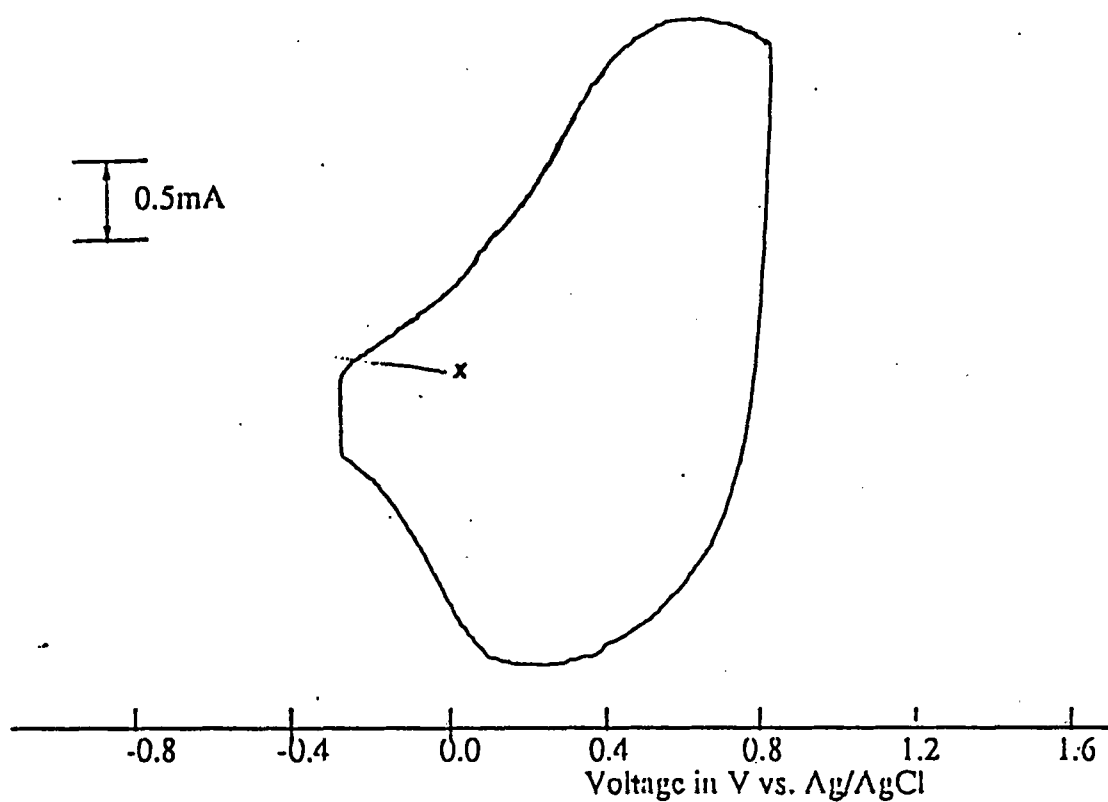


Figure 4-17 Cyclic voltammogram of PITN formed on a Platinum working electrode in 0.01M TENBF acetonitrile. Scan rate: 40 mv/s.

shown in Figure 4-8. Similarly there was only one redox wave with PITN but two redox waves with PDMITN.

The polymer film was electroactively reversible and very stable in this sweep range. A remarkable colour change was clearly observed from blue in the reduced state to slightly-yellow transparent in the oxidised state. This is consistent with that reported by Wudl<sup>4</sup>. When the relationship between the cathodic peak ( $I_p^c$ ) and potential sweep rate ( $v$ ) was examined, it was found that  $I_p^c$  was linearly proportional to  $v$  and the ratio of  $I_p^c/v$  was almost constant as shown in Figure 4-18.

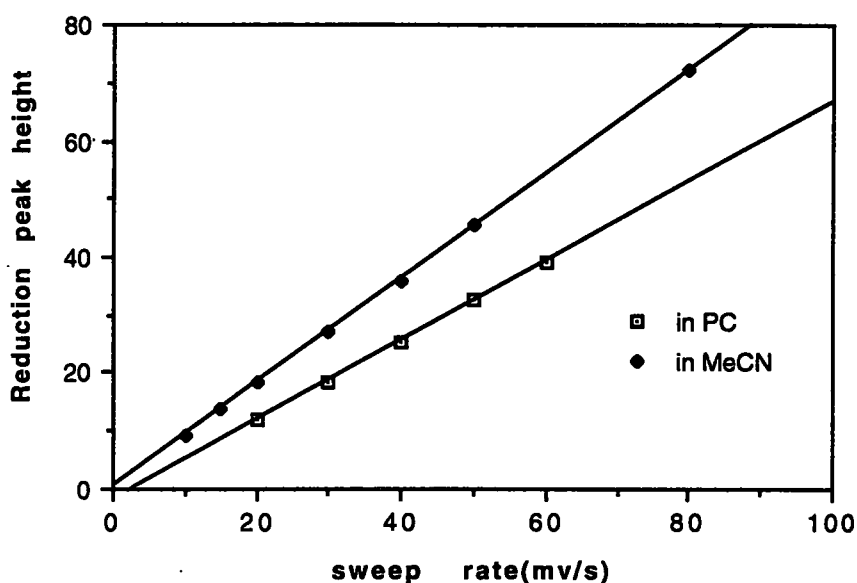


Figure 4-18 Dependence of the cathodic peak current on potential scan rate for a PITN film in propylene carbonate(PC) and acetonitrile (MeCN) solution respectively (other conditions are the same as shown in Figure 4-19 a and b)

In propylene carbonate the redox activity of the polymer film gave an almost symmetrical cathodic and anodic wave with identical peak potentials and currents(Figure 4-19b). Thus, the redox wave was even more narrow, 0.10v, with the oxidation peak at 0.50v and the reduction peak at 0.40v. On varying the potential sweep rates the peak positions of the film in both oxidised and reduced forms did not change. The cyclic voltammograms

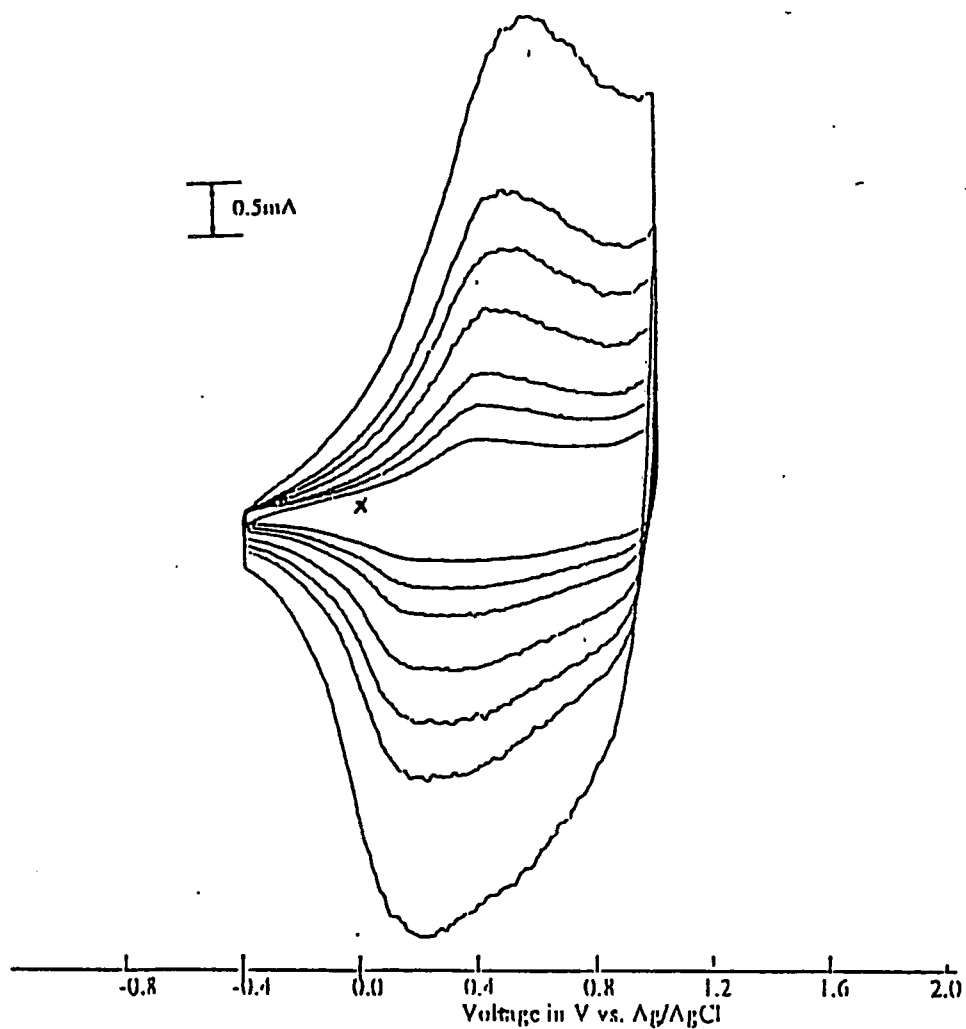


Figure 4-19a Cyclic voltammograms of PITN at different scan rates of 10, 15, 20, 30, 40, 50 and 80  $\text{mV/s}$  respectively, on a Platinum working electrode in 0.01M TENBF acetonitrile.

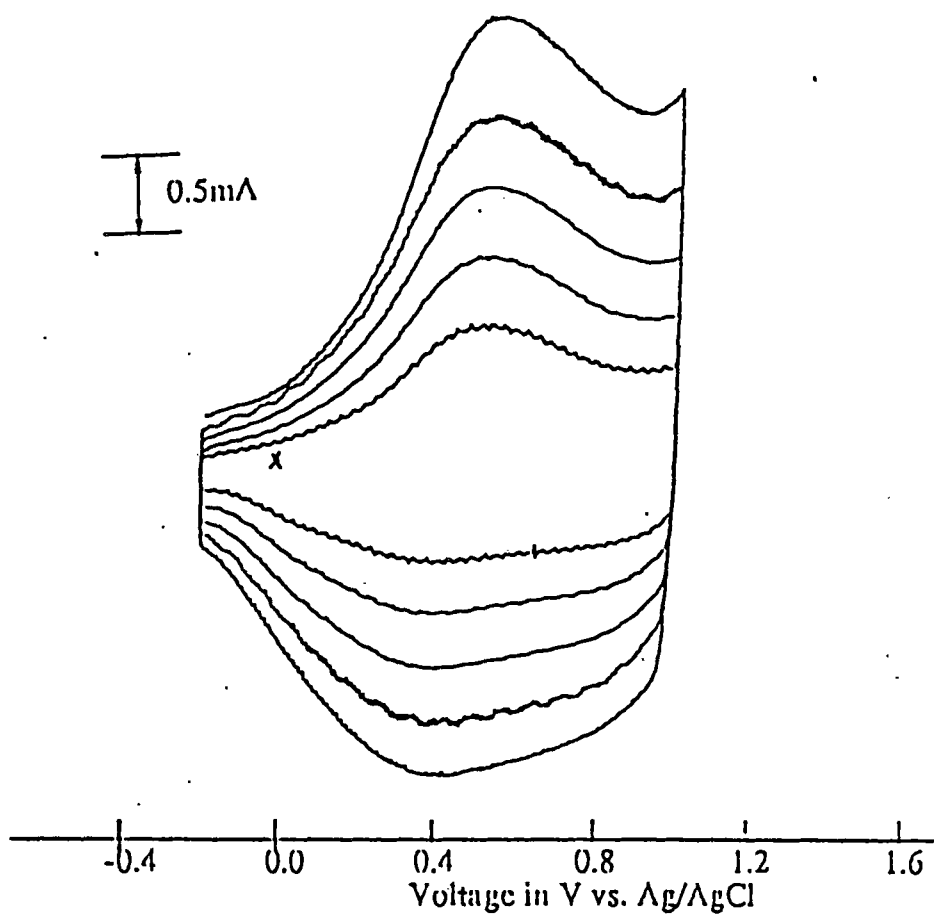


Figure 4-19b Cyclic voltammograms of PITN at different scan rates of 20, 30, 40, 60, 80 mv/s respectively, on a Platinum working electrode in 0.01M TENBF propylene carbonate.

were not completely symmetrical, with mirror-image redox waves<sup>21</sup> due to the kinetic effect of slow heterogenous charge transfer as predicted theoretically<sup>22,23</sup>. Comparison with the cyclic voltammogram of PDMITN suggests that the film made from ITN may contain less oligomers and less irregular structures. One disadvantage of the PITN film was that the potential sweep range could not exceed 1.10v, otherwise, the film become overcharged and started degrading. Over this increased potential range the cyclic voltammograms of the film were not stable and not reversible. The film was broken down after a couple of cycles. The potential sweep range of the PITN is narrower than that of the PDMITN film.

## **2) Polymers formed from DHITN**

A high quality polymer film from the dihydro-compound, DHITN, was only formed on an ITO electrode in the presence of relatively high concentrations of the monomer (0.2M) and TBNBr electrolyte(0.2M). Under other conditions the polymer film was poor and fragile. Figures 4-20 and 4-21 show that the cyclic voltammograms of the film formed from DHITN are identical to that of the film made from ITN. The oxidation peak was at 0.50v and the reduction peak was at 0.30v. The colour change from blue(neutral form) to slight-yellow transparent(oxidised form) was also observed. Due to the relative thickness of the film which was formed, the positions of the redox peaks were shifted on increasing the potential sweep rate. This shift of redox positions was caused by a slower charge transfer rate. However, there was still a good linear relationship between  $I_p^c$  and  $v$ . These results confirm that DHITN as well as ITN can be polymerised to an electroactive polymer and that the electrochemical features of both polymers were identical.

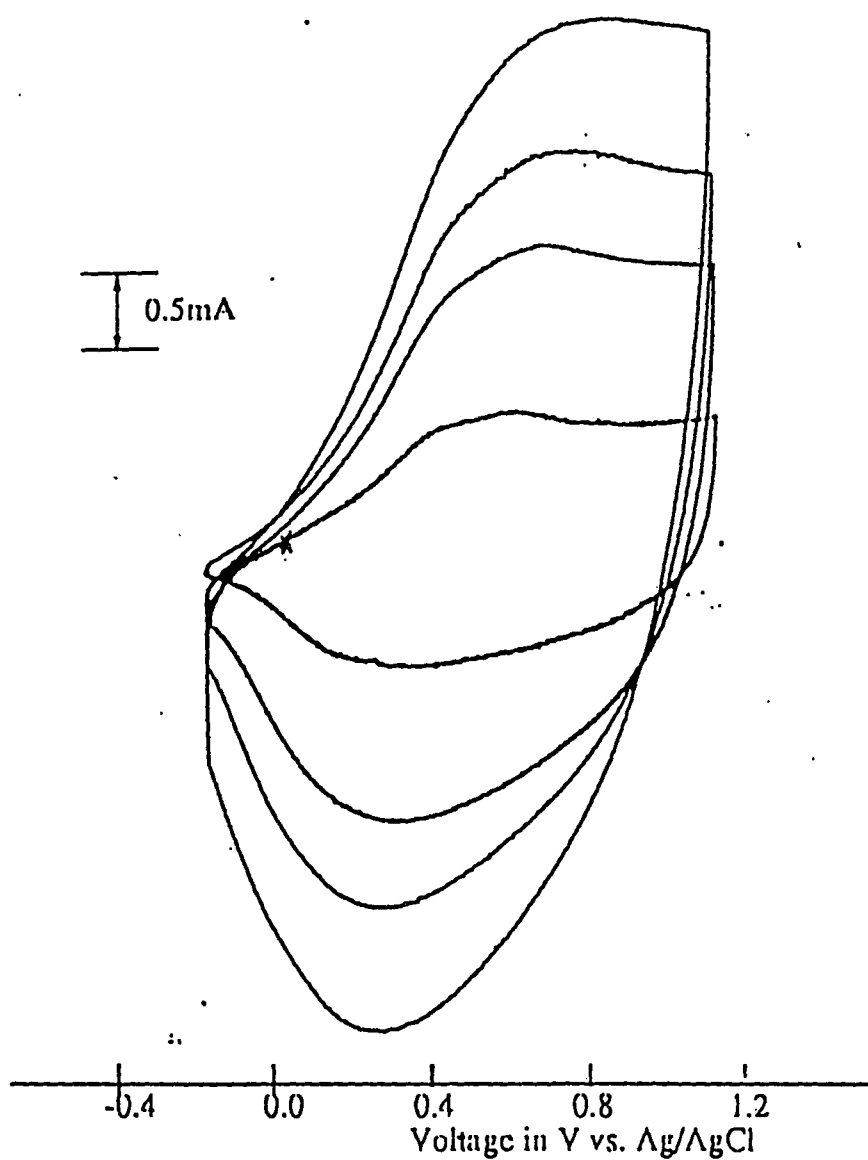


Figure 4-20 Cyclic voltammograms of PITN made from DHITN, at different scan rates of 2, 5, 7 and 100 mV/s respectively, on an ITO working electrode in 0.01M TEBF acetonitrile.



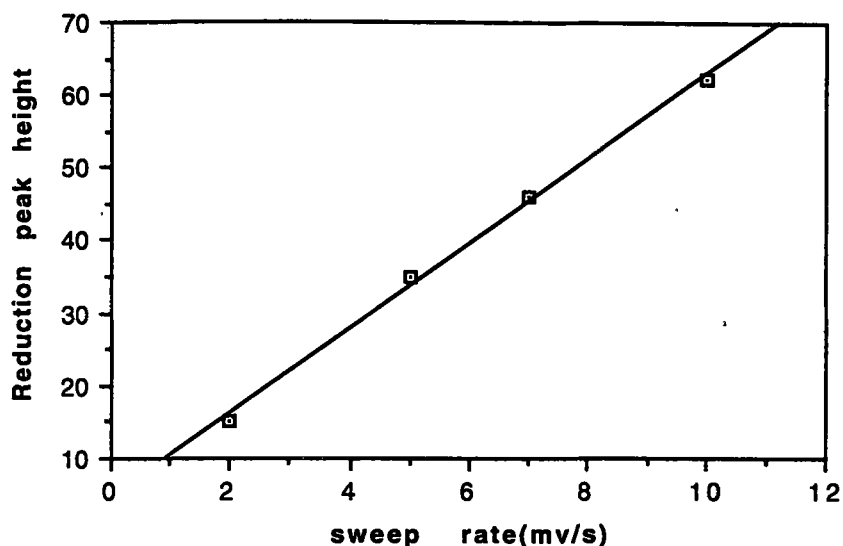


Figure 5-21 Dependence of the cathodic peak current on potential scan rate for a film PITN made from DHITN on an ITO electrode in 0.2M TBNBr acetonitrile

## 4.5 Cyclic Voltammetric Study of MeOITN, MeODHITN and Their Polymers

So far there have been no publications concerning the electrochemistry of this compound. This section discusses the cyclic voltammograms of both MeOITN and MeODHITN.

### 4.5.1 Cyclic voltammogram of MeOITN

Figure 4-22 shows the cyclic voltammograms of MeOITN on an ITO electrode in acetonitrile in the presence of TENBF. The redox wave builds up on potential cycling. The oxidation peak is at  $\sim 0.80\text{v}$  and the reduction peak at  $\sim 0.40\text{v}$ . Both peaks shifted slightly owing to the IR(voltage) drop with formation of the polymer film on the working electrode. The build up of the redox wave is undoubtedly due to the growth of an electroactive polymer film. This was confirmed by examination of the reaction cell. A coloured product (polymer film) was deposited on the electrode after the

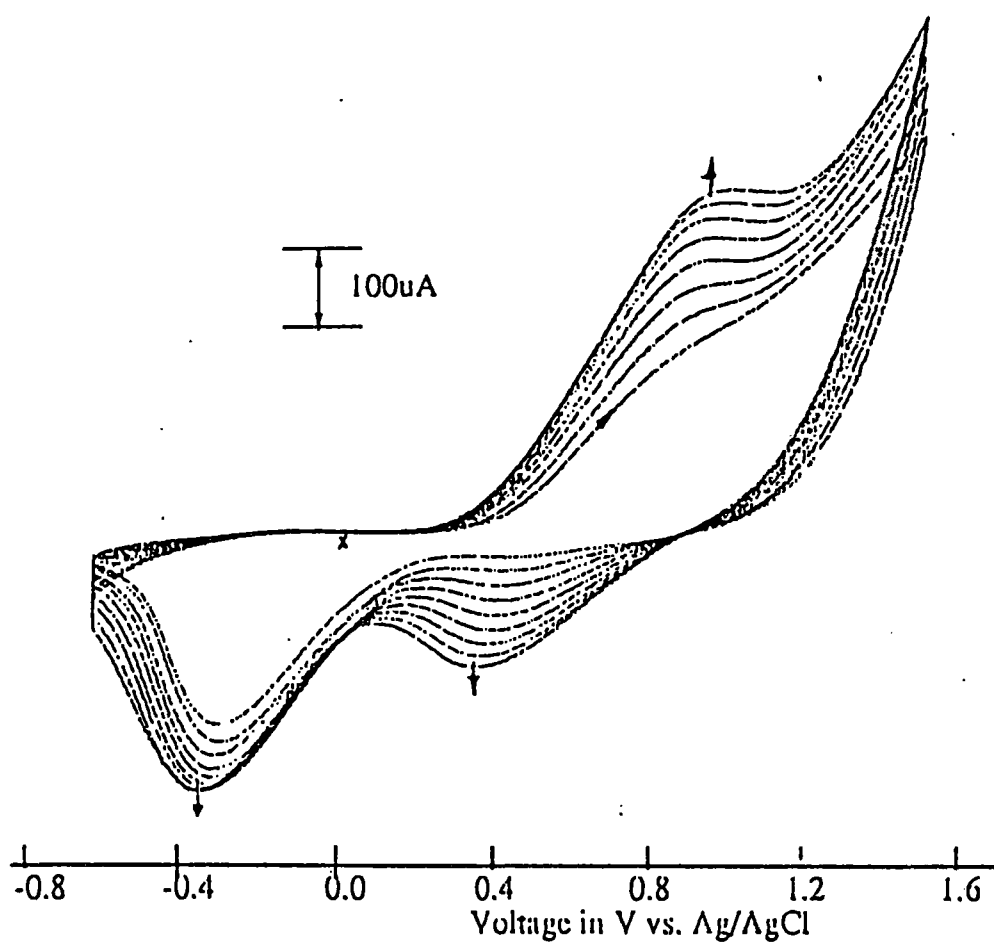


Figure 4-22 Successive cyclic voltammograms for the oxidation of 0.001M MeOITN at an ITO working electrode in 0.01M TENBF acetonitrile. Scan rate: 10  $\text{mV/s}$  (from the second to the ninth cycle).

second cycle. The colour of the oxidised polymer film was green-blue at first but become black after a series of cycles owing to the thickness of the polymer. The reduced form was brown. During the first 20 cycles the solution in the cell remained colourless with little extrusion of colour from the electrode into the solution. The pink coloured species was not observed. This seems that in this case the radical cations of the dimers, trimers etc are more reactive such that further reaction occurs before they have the opportunity to diffuse away from the electrode. This may be because the 4 substituent prevents coplanarity of the  $\pi$  system of the monomer units such that the radical cation is more localised and thus more reactive. This behaviour is very different to that of DMITN. The dimethyl groups are in the 5 and 6 positions and thus there is less interference such that they can stabilise the resulting radical cation and diminish the coupling rate. Therefore, with both ITN and DMITN, polymer films were not formed under these conditions, instead, relatively stable intermediates were formed which reacted further in solution. The confirmation of intermediate species formed from ITN and DMITN will be discussed in the next chapter.

When the solvent was replaced with dichloromethane, the cyclic voltammogram was different from that in acetonitrile as shown in Figure 4-23. The reduction peak increased slowly, but the anodic waves, with one peak and a shoulder built up more rapidly. This behaviour could be caused by the dissolution of the resulting polymer film in solution when in the neutral state. Thus, by the time the potential returned the cathodic side, part of the polymer film had already dissolved away into the dichloromethane solution, so that the reduction peak of the polymer was very weak. A blue species diffusing away from the electrode into the solution could clearly be seen.

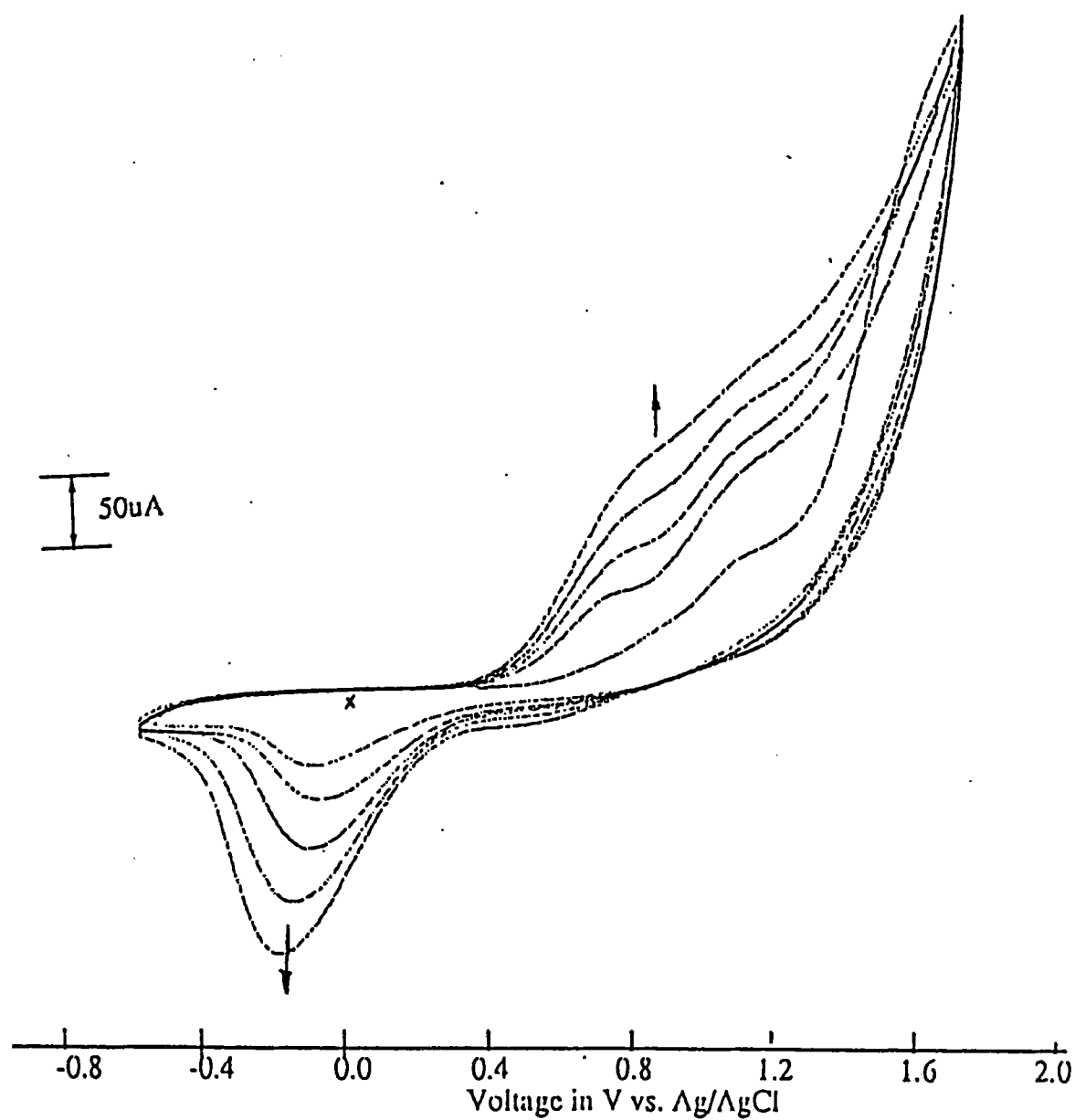


Figure 4-23 Successive cyclic voltammograms for the oxidation of 0.001M MeOITN at an ITO working electrode in 0.01M TENBF dichloromethane. Scan rate: 10 mv/s (from the first to the fifth cycle).

When a nucleophilic electrolyte, such as TBNBr, was used, only oxidation of TBNBr was observed. One explanation as to why no MeOITN polymer film is formed on the ITO electrode when TBNBr was used as a supporting electrolyte is that the radical cation of the monomer may quickly react with the oxidised TBNBr to form byproducts. At the end of the reaction the soluble product was examined by NMR. Whilst the methoxy peak remained, the peak associated with the hydrogens at C<sub>1</sub> and C<sub>3</sub> were much weaker. This indicates that only some of the monomer remained. A range of unidentified peaks in the <sup>1</sup>H and <sup>13</sup>C spectra could be seen. Although the by-products were not characterised, some side-reaction of the monomer with TBNBr must occur to inhibit the formation of the MeOITN polymer. It seems that to obtain a high quality polymer film there must be a delicate balance between the reactivity and its stability of the radical cation species. These results show that a single methoxy group at position 4 of the isothianaphthene ring has a different effect to two alkoxy groups at positions 5 and 6. Ikenoue and coworkers<sup>24</sup> found that with 5,6-dioxymethyleneisothianaphthene, the dioxole group at positions 5 and 6 of the isothianaphthene ring did not affect the polymerisation process with the nucleophilic supporting electrolyte, tetraphenylphosphonium chloride.

#### **4.5.2 Cyclic voltammogram of MeODHITN**

MeODHITN could be converted into a brown coloured soluble electroactive polymer by anodic electrolysis in the presence of non-nucleophilic supporting electrolytes such as TBNPF and TENBF. Figures 4-24 shows the cyclic voltammogram of the monomer using a Platinum electrode in acetonitrile. One oxidation peak at ~1.30v was seen. This irreversible anodic peak corresponds to the oxidation of the monomer. The redox peak of the resulting polymer was hardly visible. After about 20 cycles a film was formed on the electrode. Owing to the 'nonaromatic' structure of the

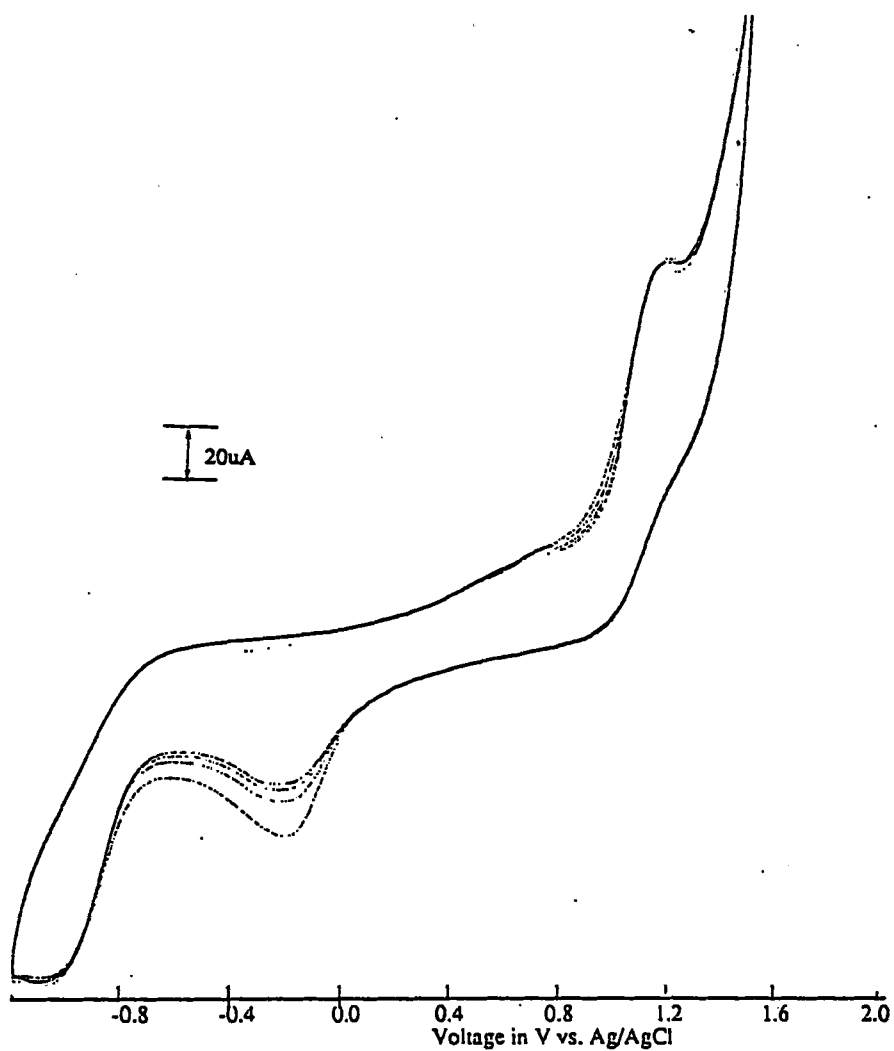


Figure 4-24 Successive cyclic voltammograms for the oxidation of 0.001M MeODHITN at a Platinum working electrode in 0.01M TENBF acetonitrile. Scan rate: 10 mv/s (from the first to the fourth cycle).

monomer (the 1,3-dihydro compound), the deposition rate of the film on the electrode was much slower than with MeOITN. Nevertheless, a polymer film could be formed during potential cycling. No pink coloured species were produced in the reaction. A thick, free standing film could be made, which resembled a sponge, if a high concentration (0.2M) of the monomer and supporting electrolyte was used.

#### **4.5.3 Cyclic voltammogram of poly(4-methoxyisothianaphthene)**

Figure 4-25 shows the cyclic voltammogram of a preformed film of polyMeOITN on an ITO electrode using TENBF in acetonitrile. The oxidation and reduction peaks occurred at  $\sim 0.80\text{v}$  and  $0.4\text{v}$  respectively, the same position obtained when the polymer was generated from the monomer. The film was green-blue in the oxidised form and brown in the reduced form. This indicates that the preformed polymer film undergoes reversible optical and electrochemical change. However, the PMeOITN film was unstable and the electroactivity of the film decreased to 50% after 20 scans from  $-0.4$  to  $1.2\text{v}$ .

Unlike PITN and PDMITN, a strong colour change was not observed with the polyMeOITN film. This confirms that the methoxy group at position 4 of an isothianaphthene ring enlarges the energy gap. This may result from distortion of the conjugated chain of polyMeOITN which affects the coplanarity of the polymer chain. This diminishes the effective conjugation length so that the energy gap between the covalent band and conduction band increases.

When a wider potential sweep range from  $-0.60\text{v}$  to  $1.50\text{v}$  was applied, a strong anodic current built up over  $1.20\text{v}$  and an extra reduction peak at  $-0.10\text{v}$  was observed. The redox peak wave was very unstable and decayed sharply with subsequent cycles. It seems that when the potential sweep is

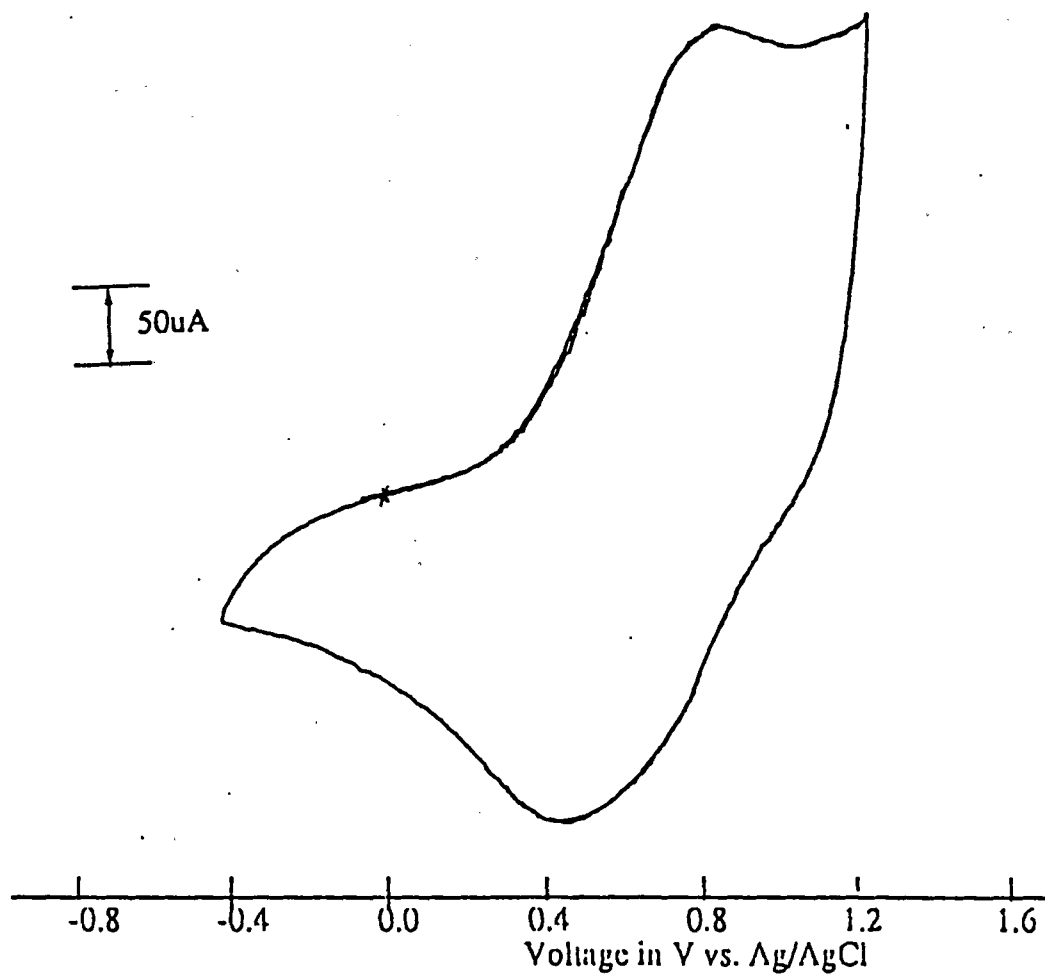
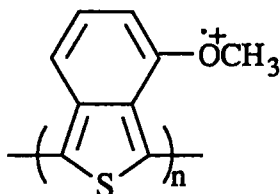


Figure 4-25 Cyclic voltammogram of PMeOITN on an ITO working electrode in 0.01M TENBF acetonitrile. Scan rate: 10 mv/s



over 1.20v a Wurster-type radical cation<sup>25</sup> may be produced by the over-oxidation of polyMeOITN, as shown below.



This may affect the redox processes of the polymer. In Chapter three we discussed how polyMeOITN formed directly by anodic electrolysis, was most likely to be found in the neutral state (brown) rather than in its oxidised state (blue-black). This was unusual since electropolymerisation normally leads to an oxidised, conducting polymer. This indicates that the oxidised state of PMeOITN may be very unstable.

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# Chapter Five

## UV/Vis Absorption Spectral Study and Chromatographic Study of Oxidative Polymerisation of Isothianaphthenes

### 5.1 Introduction

Many conducting polymers can be prepared by anodic electrolysis and chemical oxidation. Radical cation coupling and deprotonation are thought to be the general pathway for the polymerisation<sup>1-3</sup>. However, the mechanism of radical cation coupling of aromatics to form conjugated long chain polymers has not been completely elucidated. Wudl<sup>4</sup> and coworkers reported that a highly conducting isothianaphthene polymer could only be obtained in the presence of nucleophilic supporting electrolytes such as Cl<sup>-</sup> or Br<sup>-</sup>. The results from this work are in agreement with their conclusion for isothianaphthene and dimethylisothianaphthene. However, the 4-methoxyisothianaphthene gave no polymer when a nucleophilic anion(Br<sup>-</sup>) was present. Based on the FT-IR spectra of the resulting polymer Wudl suggested that an unconjugated polydihydroisothianaphthene may be formed when non-nucleophilic electrolytes, such as TENBF and TBNPF, are used. The solid state NMR, FT-IR and cyclic voltammograms in this work indicate that the formation of a long chain unconjugated polymer is unlikely. We suggest that in the presence of non-nucleophilic electrolytes the corresponding oligomer and short chain polymers predominate. So far, there have been few studies on the mechanism of oxidative polymerisation of isothianaphthene under different conditions. From a comparison with the bithiophene system Hillman and coworkers<sup>5</sup> here proposed that oligomers could be formed. In this work the discovery of a pink species, which diffuses away from the electrode and the results of the cyclic voltammetry in

the presence of tetrafluoroborate anions indicate that stable intermediates are indeed formed in the system. The good solubility and stability of the intermediates in dichloromethane offers a unique opportunity to monitor the oxidative process by time-resolved UV/Vis absorption spectroscopy and chromatographic techniques. The consumption rate of monomers, formation of intermediates and further conversion of the intermediates have been investigated and are reported in this chapter.

## **5.2 Consumption of Monomers and Formation of Intermediates**

Diaz has proposed that the polymerisation of heterocyclic aromatic compounds such as thiophene and pyrrole is a coupled chemical reaction (ECE reaction)<sup>8</sup>. Such a reaction involves a rather complex set of reactions. The relative rates of all the individual steps including the diffusion steps, the electron transfers and pure chemical reactions need to be considered. The electropolymerisation process is also a heterogeneous reaction involving the formation of a new phase, the polymer, on the electrode. Thus, it is difficult to study the reaction kinetics precisely. In this study we only concerned ourselves with the change in concentration of the monomers, and any observable intermediates. The rate of monomer consumption, and intermediate formation during polymerisation were determined using HPLC by analysing samples of the electrolysis solution, carried out at a given constant potential or constant current. If the reaction is zeroth order, then a linear relationship will be present between the concentration of monomer and reaction time. However, if the reaction is first order, the logarithm of the concentration of the monomer is linearly proportional to the reaction time.

### 5.2.1 'Fully aromatic' isothianaphthene derivatives

#### 1) DMITN

The monomer and its corresponding intermediates were very soluble in dichloromethane when the concentration of the monomer and the supporting electrolyte were below  $10^{-2}\text{M}$ . The rate of monomer depletion was measured to below 50% of its original concentration. It was noted that the reaction took less than 5 minutes before the concentration of the monomer was below 50% of its original value irrespective of the conditions applied. In the presence of a non-nucleophilic supporting electrolyte (TENBF), there was no deposit on the electrode and a pink soluble species diffused away into the solution. A typical current curve of an electrochemical reaction is shown in Figure 5-1. After quickly reaching a peak the current decays to a plateau while the reactant is being consumed.

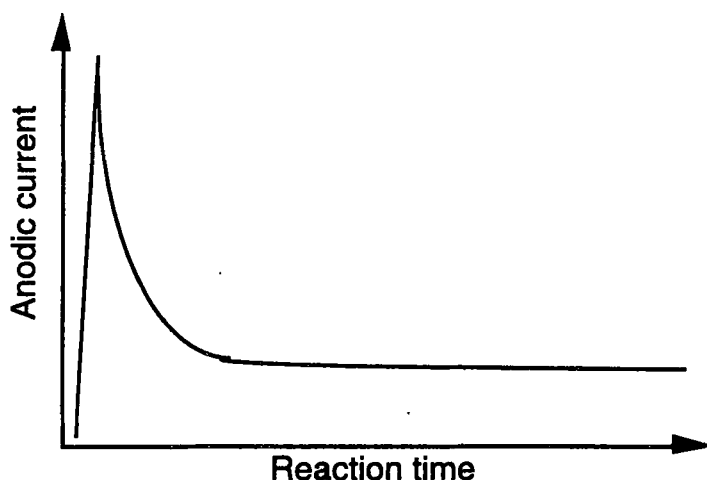


Figure 5-1 Current decay during the electrooxidation of DMITN in the presence of TENBF at a constant potential

The relationship between the concentration of the monomer and the reaction time at a constant potential (2.2v) is shown in Figure 5-2. The logarithm of the concentration of the monomer is more linearly proportional to the reaction time compared with the direct plot of the concentration of DMITN against time. Thus, this seems to be a first order reaction, that is in the

expression rate,  $(d[M]/dt) = k[M]^n$ , (where  $[M]$  = monomer concentration,  $k$  = rate constant and  $n$  = order of the reaction)  $n$  equals one.

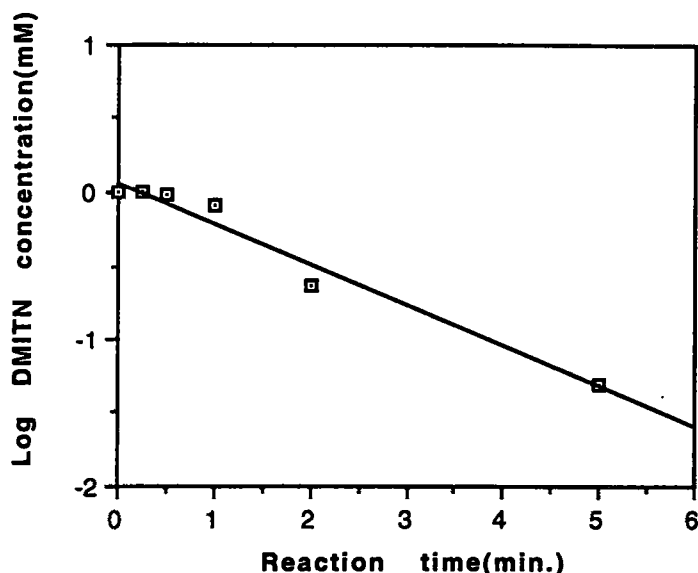


Figure 5-2 First-order plot of log [DMITN] against time during electrooxidation at 2.2v in 0.01M TENBF dichloromethane (to over 50% conversion)

On the macroscopic scale, since the solution is stirred during the electrolysis, the reaction could be considered to be diffusion controlled, that is, the mass transport becomes the rate determining step. Furthermore, the mass transport (diffusion rate) is a function of potential<sup>6</sup>. So the reaction potential should directly affect the rate of consumption of the monomer. Figure 5-3 shows that when different potentials or currents were applied at 1.8v, 2.2v, 2.8v and 2.0mA respectively, the observed rate constant changed but the first order behaviour remained. The rate of consumption of the monomer was higher, the higher the applied potential, causing the surface concentration of the monomer to decrease rapidly and the diffusion rate to increase. When a constant current was applied at 2.0 mA/cm<sup>2</sup> the depletion of the monomer also showed first order behaviour against reaction time.

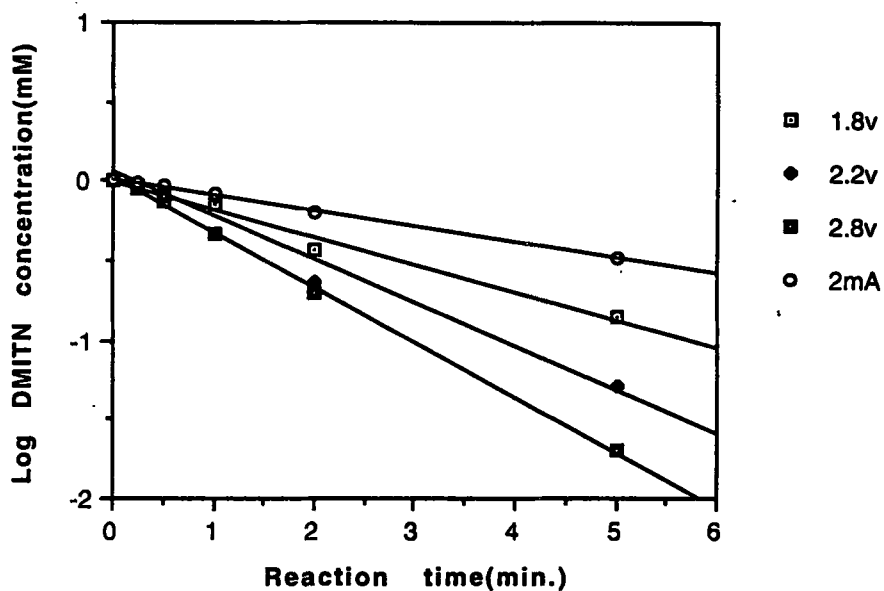


Figure 5-3 Effect of applied potential and current on consumption rate of DMITN during electrooxidation in 0.01M TENBF dichloromethane (to over 50% conversion)

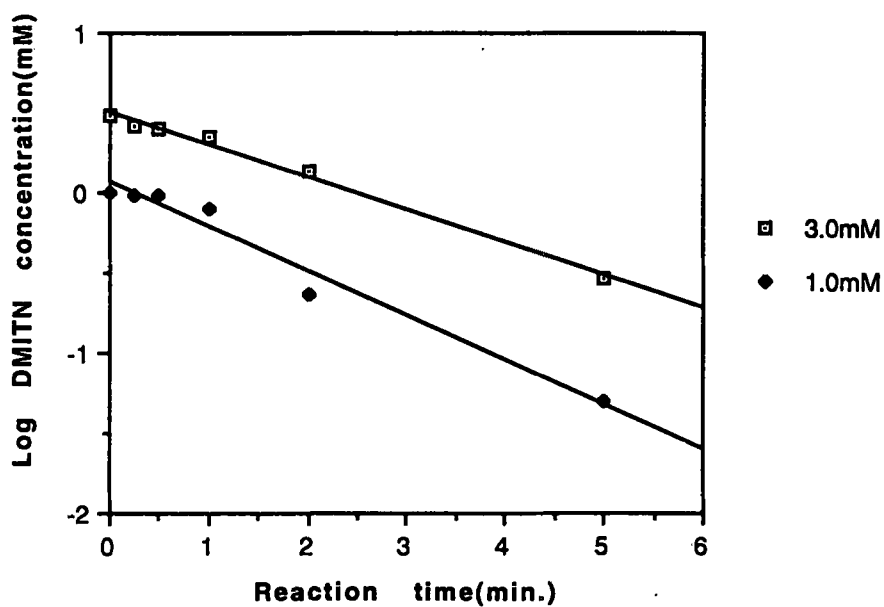


Figure 5-4 Effect of starting concentration(DMITN) during electrooxidation at 2.2v in 0.01M TENBF dichloromethane (to over 50% conversion)



This feature could be easily explained in terms of the number of faradays passing during a given period. A high applied potential leads to a high amount of charge passing through the reaction cell. This is consistent with traditional electrochemical kinetics in which rate constants vary with the potential difference at the electrode surface during electron transfer<sup>7</sup>.

To examine the effect of initial concentration of the monomer on the reaction rate two concentrations of 0.001M and 0.003M were selected. At both concentrations the reaction order and the rate constant were identical. Figure 5-4 shows two nearly parallel straight lines (logarithm of concentration against reaction time). This again confirms that the reaction is roughly first order.

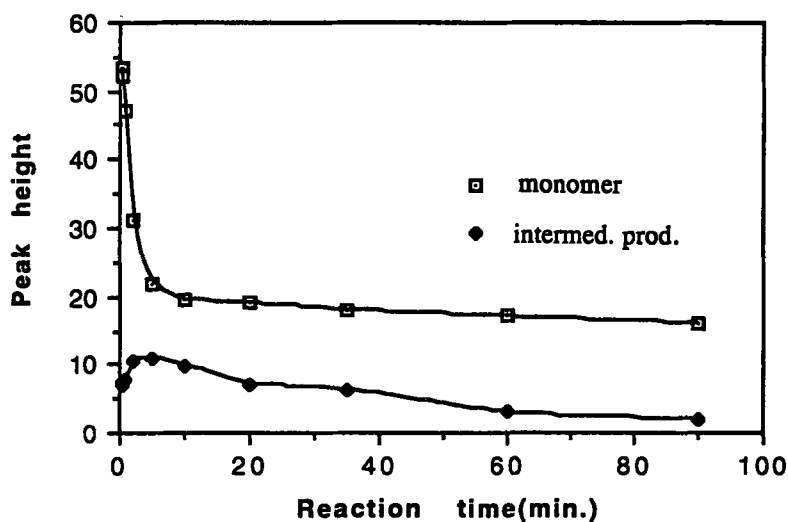


Figure 5-5 Changes in the concentration of DMITN and a corresponding intermediate during electrooxidation at 2.2v in 0.01M TENBF dichloromethane

HPLC showed that in addition to the monomer peak there were several other peaks. The peak which eluted immediately after the monomer peak could be quantitatively measured as shown in Figure 5-5. This intermediate species is thought to be a very short chain oligomer, most likely a dimer, since the

retention time is very close to the retention time of the monomer. Further clarification of the structure of this intermediate species could be achieved using an electrospectral study. However, this species has not yet been fully characterised. Comparison with the depletion of the monomer showed that the peak height of the intermediate species reached a maximum when the consumption of the monomer was about 70%, then decreased as shown in Figure 5-5. This indicates that the monomer may be converted into a soluble intermediate in either the neutral or oxidised forms which diffuse away from the electrode. The intermediates could then react further in two ways: a) they could couple in the solution; b) they could be absorbed back on the electrode and further oxidised.

It was also found that, as shown in Figure 5-6, when a high potential was applied, the intermediate was formed in higher concentration. The pink colour in the reaction cell was also stronger at the high potential (2.8V). The pink coloured species and the intermediate monitored using HPLC were shown to be different. The former was an oxidised intermediate and the latter was a neutral species. A silica column was used in HPLC and this would only let the neutral species pass through. As we shall see later, the pink coloured species is most likely an oxidised species (a radical cation). Nevertheless, this indicates that the higher polymerisation potential leads to the formation of a large amount of the intermediate species in the solution. Undoubtedly, the concentration of intermediate species would affect the formation of the polymer film on the electrode and the conductivity of the product. This is perhaps why the conductivity of the isothianaphthene polymers decreased when the applied potential was high. It is also in agreement with the earlier suggestion by Diaz and coworkers<sup>8</sup>: that a higher potential leads to higher amounts of intermediate species, and the formation of a black powder rather than a high quality film. Reports<sup>5,22</sup> on the

polymerisation of ITN in the presence of a non-nucleophilic supporting electrolyte suggests that a good quality film could be produced if care is taken over the control of potential(1.1 ~ 1.2v vs. SCE). Thus, we conclude that a high conducting polymer can be made if the concentration of the intermediate species is kept low by controlling the applied potential.

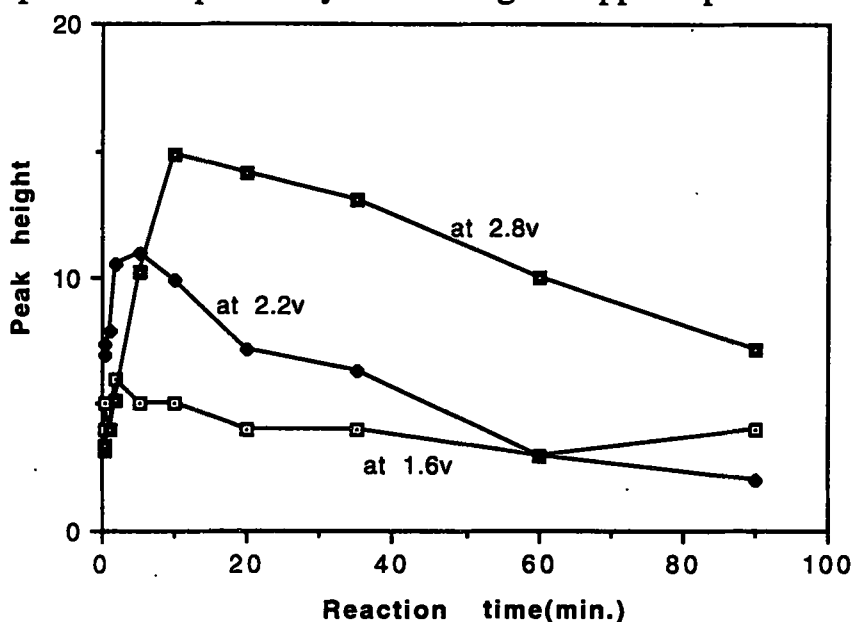


Figure 5-6 Effect of applied potential on concentration of the corresponding intermediate during the electro-oxidation of 0.001M DMITN in 0.01M TENBF dichloromethane

When the reaction was carried out in the air without nitrogen protection, the outcome was not significantly different. In both cases the reaction followed first order kinetics. The logarithm of the concentration of the monomer was proportional to the reaction time and the peak height of the intermediate changed with the reaction time in a similar fashion. The pink colour was also clearly noticeable in the solution for a long time. The only difference was that the apparent rate constant of monomer consumption was slightly lower under nitrogen. The results are shown in Figure 5-7. It seems that the presence of oxygen in the system may slightly accelerate the consumption of the monomer but does not fundamentally change the features of the reaction.

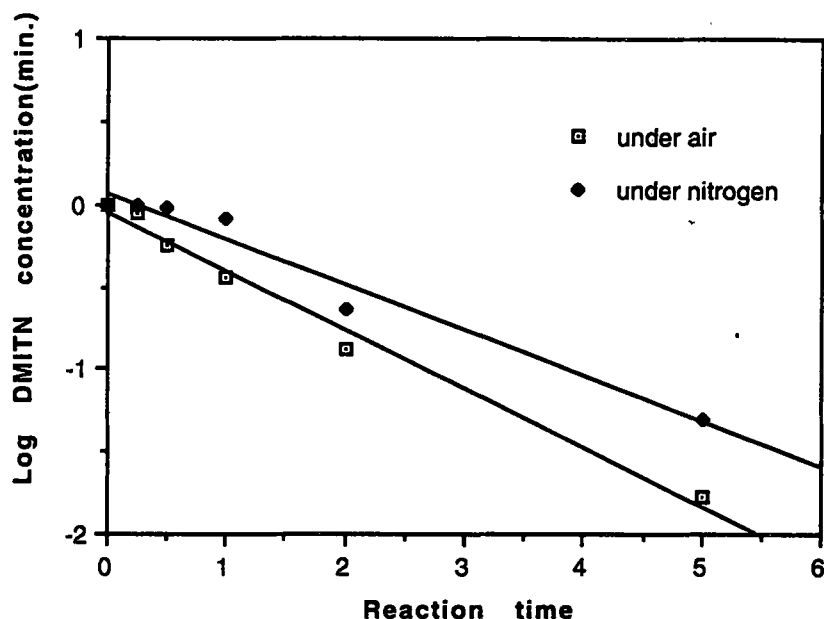


Figure 5-7 First-order plots of log [DMITN] against time during electrooxidation at 2.2V under nitrogen and oxygen respectively in 0.01M TENBF dichloromethane (to over 50% conversion)

When the non-nucleophilic supporting electrolyte(TENBF) was replaced by a nucleophilic electrolyte(TBNBr) the kinetic features of the reaction changed. Figure 5-8 shows that the reaction seems to become zeroth order. The consumption of the monomer was directly proportional to the reaction time. The peak height of the intermediate remained very low for the whole of the reaction period. The pink coloured species did not appear in the solution and the solution gradually turned slightly brown-yellow but remained transparent. A deposit could be observed on the electrode. This deposit was not soluble in the solution, unlike that formed when the tetrafluoroborate anion was used. These results suggest that in the presence of a nucleophilic supporting electrolyte (TBNBr) less soluble intermediate species are formed. This agrees with the proposal of Diaz<sup>8</sup> that a high quality polymer or film can only be obtained when less soluble intermediates are formed.

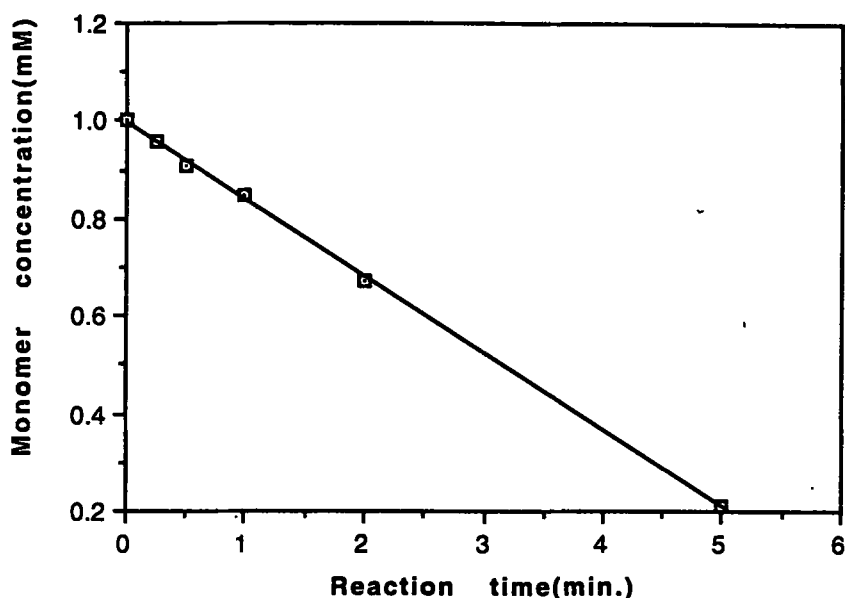


Figure 5-8 Zeroth-order plot of [DMITN] against time during electrooxidation at 2.0v in 0.01M TBNBr dichloromethane (to over 50% conversion)

However, why the use of a nucleophilic supporting electrolyte leads to the formation of a polymer film via less soluble intermediate species is not known. Conventionally, in electrochemical systems, nucleophiles inhibit the propagation steps because the radical cation, formed by electron transfer, may react with the nucleophile to form a by-product rather than the required product. In the polymerisation of heterocyclic compounds, such as thiophene and pyrrole, to obtain high conducting polymers nucleophiles should be avoided. However, in this system the presence of the nucleophilic electrolyte seems to be beneficial.

Although the reaction kinetics of DMITN consumption in the presence of TBNBr is zeroth order, the actual reaction mechanism is likely to be very complicated involving diffusion, electron transfer, chemical reaction and absorption on the formation of a new phase on the electrode surface. Furthermore, due to deposition of an electroactive polymer on the electrode, the corresponding current increased rather than decreased during the

electrochemical process. A further electrospectral investigation is described in the next section.

## 2) ITN

Previously we have described how the electropolymerisation and cyclic voltammograms of DMITN and ITN are similar. However, the polymer film from ITN exhibited better reversible electrochemical behaviour than that of DMITN. We suggested that the dimethyl groups of DMITN could stabilise the radical cation of the monomer and the corresponding intermediates, thus reducing the reactivity of the radical cation to coupling and further propagation, so that the resulting product would most likely be a mixture with some short chain oligomers.

In this section we compare the rate of consumption of ITN and the formation of its intermediates with those of DMITN. During the electropolymerisation in the presence of a non-nucleophilic supporting electrolyte(TENBF) at 2.2v vs. Ag/AgCl reference electrode, the reaction of ITN, like DMITN, exhibited approximately first order behaviour (Figure 5-9). There was a good linear relationship between the logarithm of the concentration of the monomer and the reaction time. Most of the monomer was lost during the first five minutes. The consumption rate of ITN was slightly higher than that of DMITN under the same conditions.

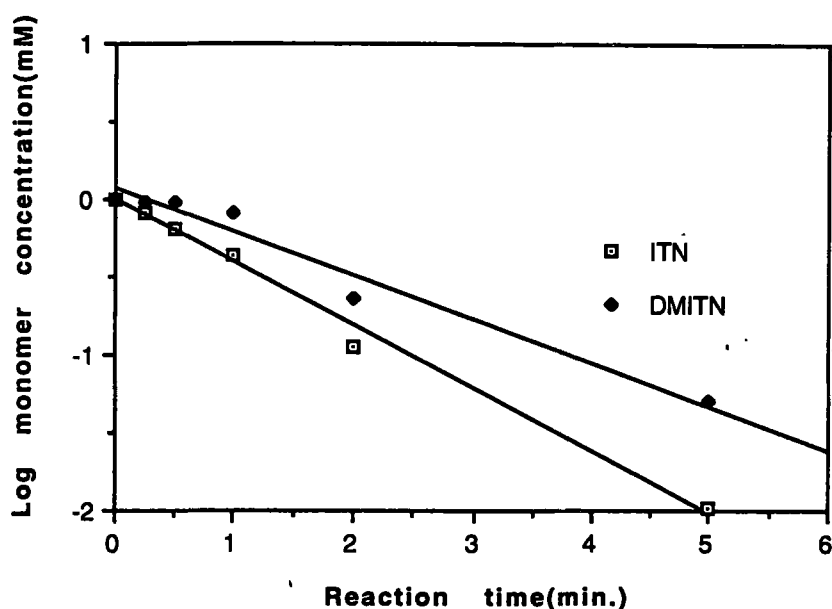


Figure 5-9 First-order plots of log [ITN] and [DMITN] against time during electrooxidation at 2.2v in 0.01M TENBF dichloromethane (to over 50% conversion)

The HPLC chromatogram contained peaks with a longer retention time than the monomer. Unfortunately, they were very weak throughout the electrolysis. Thus, it was not possible to determine any relationship between the peak height of the intermediate and the reaction time. This indicates that the concentration of the neutral intermediate at the low retention time are lower for ITN than for DMITN. In other words, the oxidised species from ITN may be more reactive undergoing coupling more readily to give longer chain oligomers.

### 3) MeOITN

Unlike the addition of two methyl groups, the introduction of a methoxy group at position 4 of ITN has a dramatic affect on the polymerisation process. 4-Methoxyisothianaphthene could only be electropolymerised in the presence of a non-nucleophilic supporting electrolyte such as TENBF. Thus, in this section only the oxidation of the monomer in TENBF was investigated. Figure 5-10 showed that the depletion of the monomer was

linearly proportional to the reaction time, that is, the reaction displayed an apparent zeroth order.

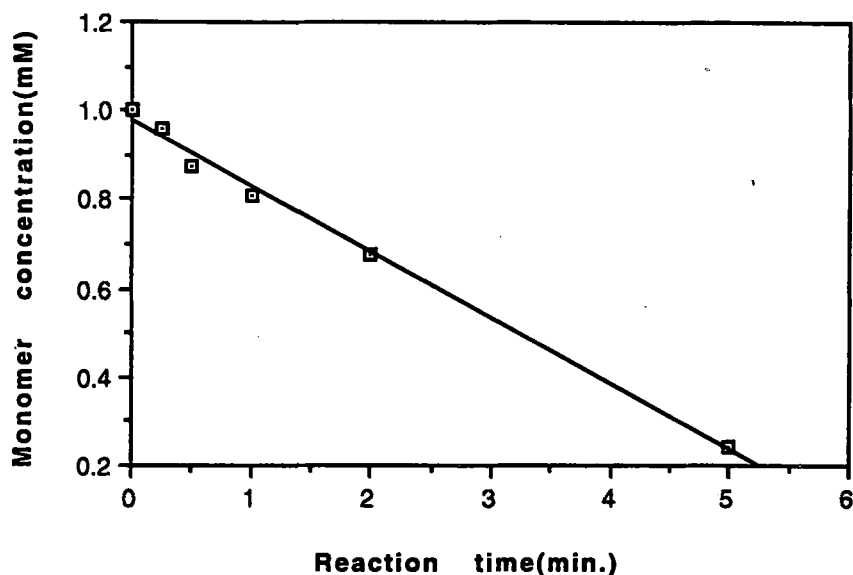


Figure 5-10 Zeroth-order plot of [MeOITN] against time during electrooxidation at 2.0v in 0.01M TENBF dichloromethane (to over 50% conversion)

In the HPLC there was no sign of any other peaks corresponding to the intermediates. This behaviour was similar to that of DMITN in the presence of TBNBr. The difference was that the polyMeOITN film formed on the electrode slowly dissolved into the dichloromethane and the solution turned slightly green-blue (the oxidised polymer was green-blue and the neutral one was brown). These two cases suggest that if a polymer is formed on the working electrode, the kinetics of oxidation of the monomer is likely to be zeroth order. The polymer film deposition may not be affected by the change in the concentration of the monomer. However, if stable soluble intermediate species are formed on the working electrode which then diffuse into the solution, the oxidation of the monomer is likely to be first order. In this case the concentration of the monomer could affect the reaction rate and the reaction seems to be diffusion controlled as in traditional electrochemical reactions.



### 5.2.2 1,3-Dihydroisothianaphthene derivatives

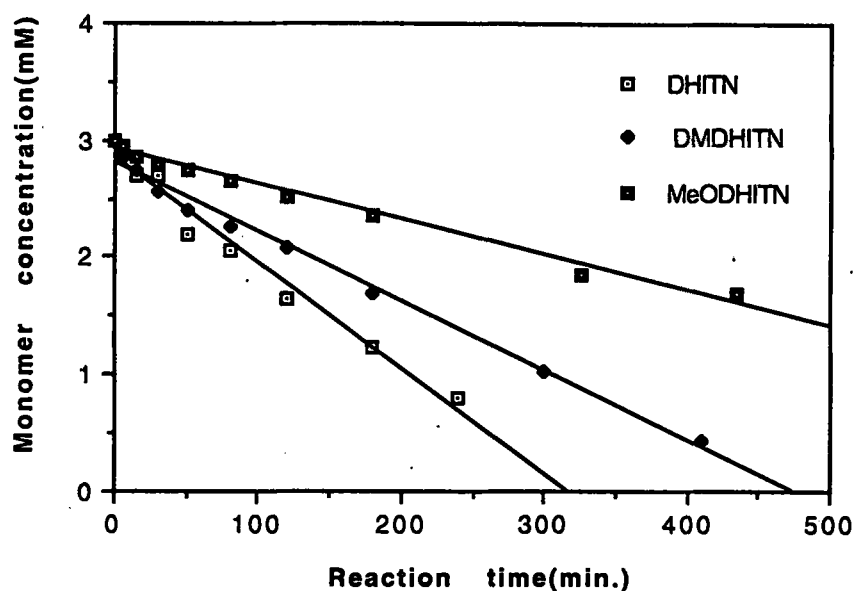


Figure 5-11 Relationship of monomer consumption with reaction time during the electrooxidation of DMDHITN, DHITN and MeODHITN respectively at 4.0mA in 0.03M TENBF dichloromethane

The polymerisation of both the fully aromatic and the 'non-aromatic' (1,3-dihydro) monomers leads to identical polymers. However, since the 1,3-dihydroisothianaphthene monomers have two extra hydrogens on C<sub>1</sub> and C<sub>3</sub>, conversion to the conjugated polymers must involve an extra deprotonation process. The polymerisation of DHITN is the first report of such an electropolymerisation and may be a result of the presence of a benzene on the thiophene ring. The conversion from monomers to polymers is thus more complex. Besides the first peak, arising from the monomer, a number of extra peaks could be observed in the HPLC. Due to the limitation of the analytic technique the species from the electrooxidation of the monomers could not be identified. These peaks may be intermediates or unwanted by-product. Thus, we only focussed on the concentration change of the monomers with time. In the polymerisation process a constant anodic current (4.0 mA/cm<sup>2</sup>) was applied and the results are shown in Figure 5-11.

## 1) DMDHITN

As expected, the rate of consumption of the monomer was much slower than that of the fully aromatic monomer. The consumption of the monomer was linearly proportional to the reaction time. This showed the oxidation of DMDHITN was zeroth order. The depletion of the monomer concentration to 50% of its original value took more than 180 minutes whereas it took less than 5 minutes with the fully aromatic DMITN. If the oxidation of the aromatic monomer DMITN involves a 2 electron transfer, the oxidation of the 'nonaromatic' monomer DMDHITN will involve theoretically a 4 electron transfer. In fact, the charge passed during the reaction was far greater than the value expected for 50% depletion of the monomer. This indicates that during the polymerisation further reactions may take place. In the HPLC a number of strong peaks could be observed, as well as that of the monomer, which increased as the reaction proceeded. If these peaks belong to intermediates, then the peak heights should first increase reach a maximum and then decrease. However, most of them continued to increase until the reaction was stopped. Thus, most of the species were thought to be by-products. This could be the reason why the yield of the polymer was below 40%. Unfortunately, these species have not yet been identified.

Although some side reactions took place to produce soluble by-products during the polymerisation they did not significantly affect the formation of the conjugated polymer. The phenomenon of the pink coloured species and the blue coloured deposit was the same as with DMITN.

## 2) DHITN

Compared with ITN, the consumption rate of DHITN was much slower and the reaction was zeroth order. The oxidation of DHITN is more complicated than that of ITN. A number of peaks could be seen in the HPLC as well as

the first peak of the monomer. Some side-reaction may have occurred during the oxidation, as with DMDHITN.

### **3) MeODHITN**

The oxidation of MeODHITN displayed zeroth order kinetics, similar to those of DMDHITN and DHITN. As expected, the consumption rate of the monomer was much slower than that of the corresponding aromatic compound.

## **5.3 The Change in The UV/Vis Absorption Spectra during Oxidative Polymerisation**

Although HPLC was able to monitor the change in the monomer concentration, examine the formation of intermediates and demonstrate the apparent kinetic features, no oxidised species(radical cations) could be identified using this technique. Spectroelectrochemistry, particularly in the UV/Vis/near-IR region<sup>9,10,11</sup>, has become a standard technique for the characterisation of electrogenerated species. This technique is very sensitive to conjugated compounds and radical ion species. Electronic absorption wavelengths can be related to the conjugation length of a compound, especially for short chain oligomers. In the oligo( $\alpha$ -thiophene)s, the values of the absorption maxima( $\lambda_{\text{max}}$ ) increases throughout the series. The UV-Visible data of the oligo( $\alpha$ -thiophene)s are summarized in Table 5-1<sup>12,13</sup>.

In addition, the radical cations of the oligo( $\alpha$ -thiophene)s have strong absorptions in the Visible and near infra-red<sup>14-20</sup>. During the polymerisation of the parent thiophene the reaction is so fast that the insoluble polymer is immediately formed on the working electrode and no intermediate species could be found in solution. Thus, attention has switched towards examining a series of oligo( $\alpha$ -thiophene)s as model compounds.

Due to their solubility the resulting radical cations could be observed using UV/Vis spectroscopy. The oxidation of polythiophene from a polaron to a bipolaron state could be partly confirmed by investigating the oxidation process of its oligomers. Our current work has the unique advantage that in the presence of non-nucleophilic supporting electrolytes a range of soluble intermediates in both neutral and oxidised states are formed, which are relatively stable. This offers the opportunity to monitor the oxidation process of isothianaphthene derivatives in both electrochemical and pure chemical conditions by absorption spectroscopy.

Table 5-1 UV/Vis absorption spectral data of thiophene oligomer

| no. of thiophene unit | $\lambda_{\text{max}}$ , nm | $\epsilon_{\text{max}}$ , $\times 10^{-4}$ |
|-----------------------|-----------------------------|--|
| 1                     | 248                         | 1.08                                       |
| 2                     | 305                         | 1.74                                       |
| 3                     | 360                         | 2.72                                       |
| 4                     | 391                         | 3.45                                       |
| 5                     | 416                         | 3.69                                       |
| 6                     | 438                         | 4.06                                       |
| 7                     | 440                         | 4.13                                       |

### 5.3.1 UV/Vis absorption spectral study of the electrochemical oxidation of isothianaphthene Derivatives

#### 1) DMITN and DMDHITN

Figure 5-12 shows the spectral changes that occur for solutions of DMITN in the presence of TENBF upon oxidation at a constant potential of 2.0v in time intervals over one hour. A number of intermediate species were formed, giving absorption peaks at ~ 370, 540, 700 and 850 nm. As the electrooxidation progressed the peaks at low wavelength appeared first followed by the peaks at high wavelength. The absorbance below 400 nm increased dramatically from the onset, but the peaks at 700 and 850 nm

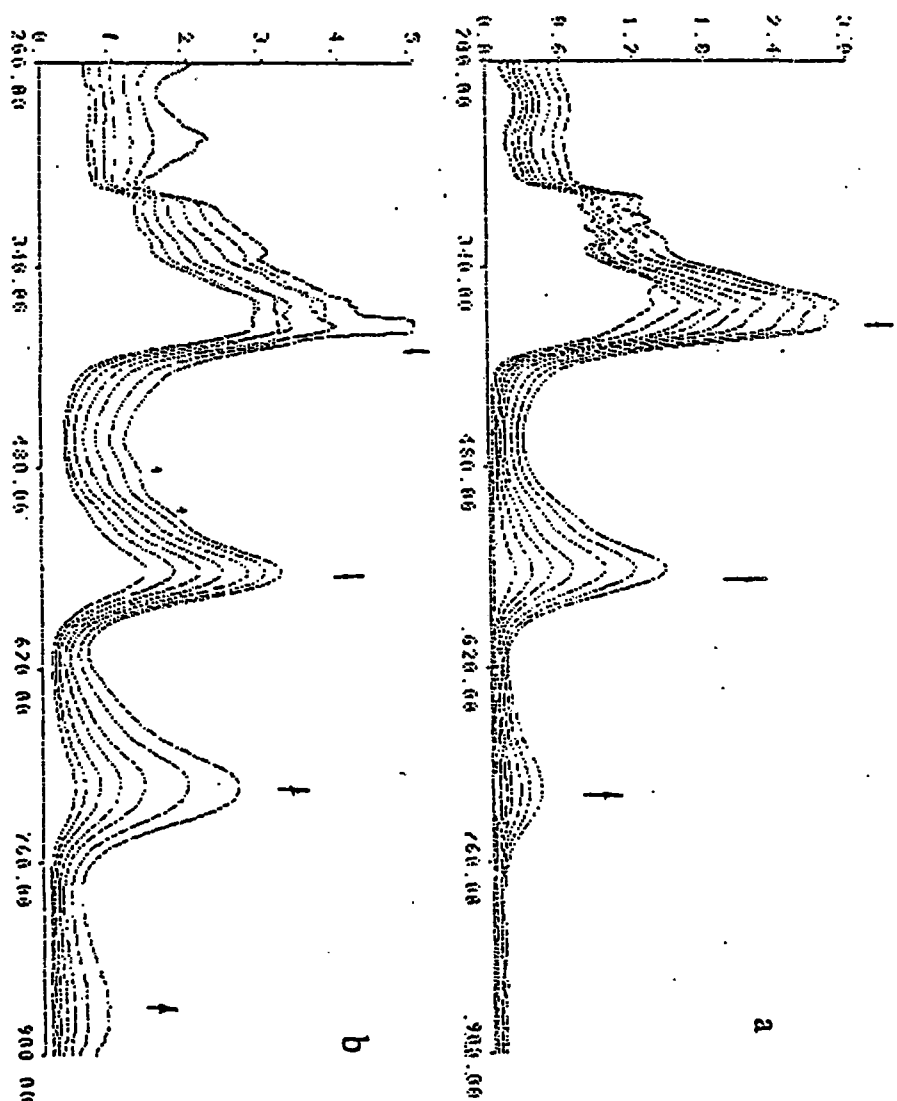


Figure 5-12 Successive UV/Vis. absorption spectra obtained during the electrooxidation of 0.001M DMITN at 2.0v in 0.01M TENBF dichloromethane. a) in 50 min. and b) from 50 to 120 min.

rosed markedly later in the reaction. Figure 5-13 shows that the height of each of the peaks at 540, 700 and 850 nm varied independently, thus, they must be separate species. Their absorptions correspond to the pink, green and blue species formed during the reaction. These species were shown to be oxidised species as will be discussed later.

Although the samples of polyDMITN in the neutral state, with different conjugated chain lengths, have electronic absorption peaks at wavelength of 525, 690 and 840nm respectively, the pink, green and blue species mentioned here could not be the final polymer, since these absorption bands disappear after reduction with diethylamine. Comparison with the radical cations of the thiophene oligomers<sup>21</sup> suggests that the absorption peaks at 540, 700 and 850nm may be attributed to radical cations of oligomers with different conjugated chain lengths(probably the dimer, tetramer and hexamer). The radical cation of the monomer could not be identified owing to its higher reactivity. The HPLC of the reaction mixture suggested that most of the monomer disappeared in the first five minutes of the reaction, however, the absorption peaks at 550, 700 and 850 nm increased steadily for more than one hour as shown in Figure 5-13.

This confirmed that these absorption bands do not arise directly from the monomer but are the presence of other intermediate species. It was also noted that the peak at 540nm appeared first followed by the peaks at 700 and 850nm successively. This may correspond to the progressive formation of more conjugated species. This also indicates that during electrooxidation, in the presence of non-nucleophilic electrolytes, a series of short chain oligomers are formed in solution rather than the unconjugated poly(1,3-dihydroisothianaphthene) as suggested by Wudl<sup>4</sup>.

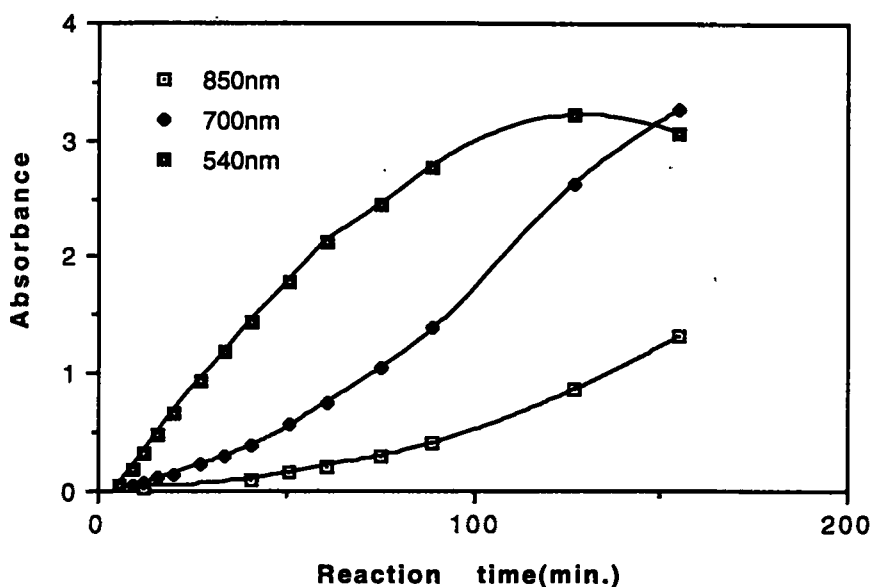


Figure 5-13 Variation of the peak absorption intensity at 540, 700 and 850 nm respectively during the electrooxidation of 0.001M DMITN at 2.0v in 0.01M TENBF dichloromethane

Careful examination of the spectra during the latter stages of the reaction revealed two absorption shoulders at 490 and 515nm. This may result from the disproportionation and coupling of the radical cations in the solution to form neutral species.

The electron absorption spectra of DMDHITN were identical to that of DMITN when the reaction was carried out under the same conditions (Figure 5-14). There were a number of absorption peaks at ~ 380, 540, 700 and 850 nm building up successively, as in the DMITN system. The difference is in the growth rates of the absorption peaks which are much slower, as shown in Figure 5-15. This suggests that the electrooxidation process is essentially the same in both cases. However, the mechanism of conversion of the 1,3-dihydro compound to the conjugated product is still unknown. The compound may first be oxidised and deprotonated by a two electron transfer to give the fully aromatic monomer on the working

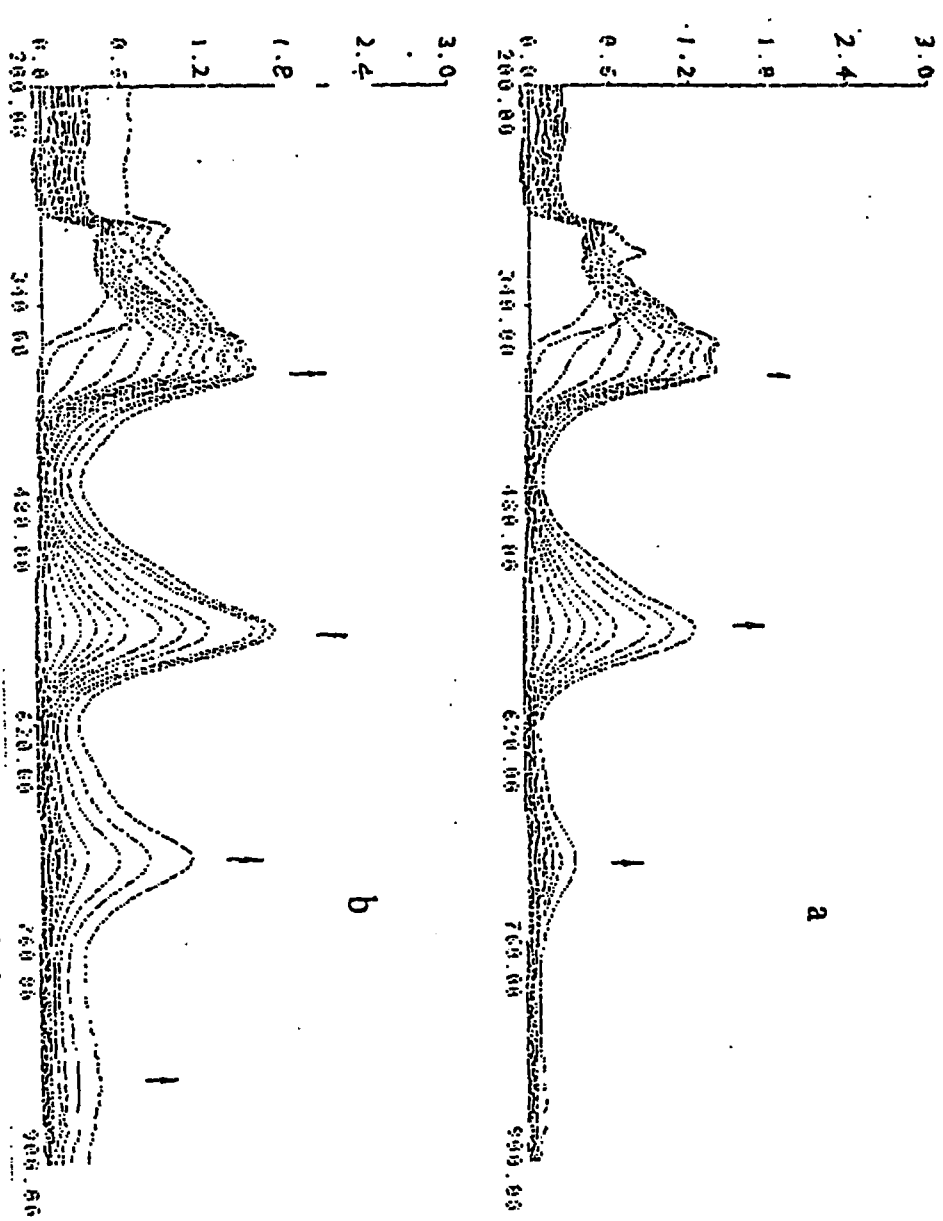
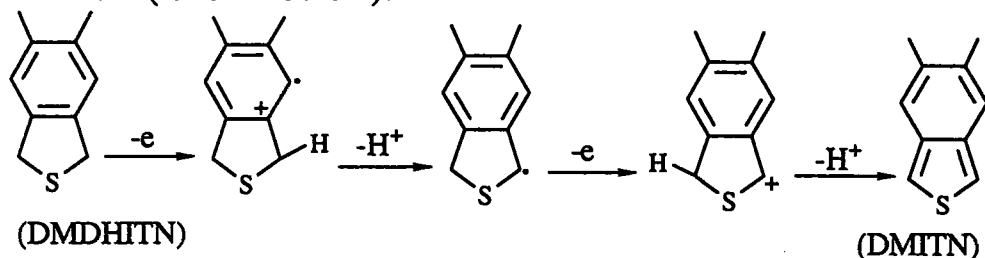


Figure 5-14 Successive UV/Vis. absorption spectra obtained during the electrooxidation of 0.001M DMDHTN at 2.0v in 0.01M TEBBF dichloromethane over 120 min.



electrode( shown below).



This could be followed by rapid further oxidation to form the same intermediate species as in the DMITN oxidation. However, the formation of DMITN from DMDHITN could not be confirmed since the resulting DMITN would be oxidised immediately on the electrode during anodic electrolysis.

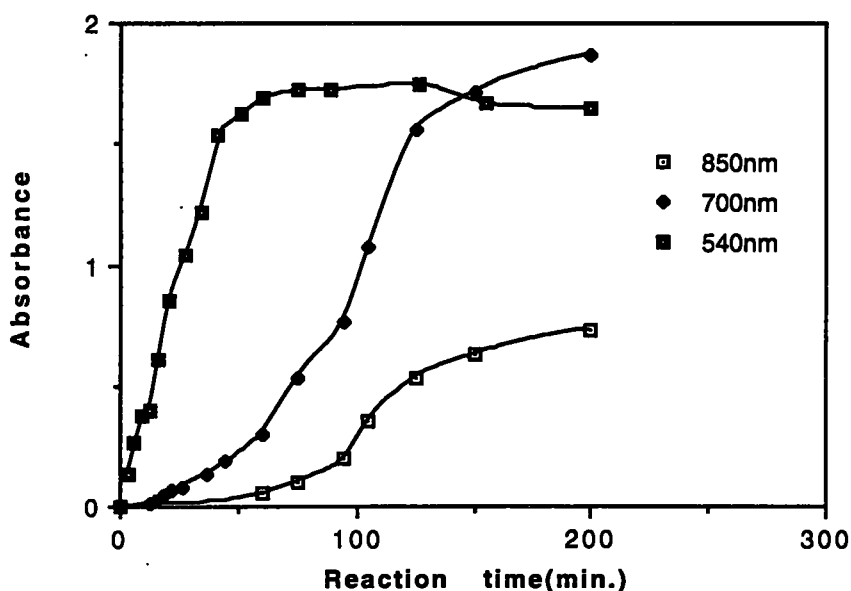


Figure 5-15 Variation of the peak absorption intensity at 540, 700 and 850 nm respectively during the electrooxidation of 0.001M DMDHITN at 2.0v in 0.01M TENBF dichloromethane

## 2) ITN and DHITN

Figure 5-16a and b shows successive electron absorption spectra acquired during the electrooxidation of ITN and DHITN at 2.0v. As the oxidation progressed the peaks at ~ 370, 540, 700 and 850 nm built up in both monomer solutions. Undoubtedly, the same intermediate species were

formed during the oxidation in both cases. However, the rate of growth of the absorption intensity at these wavelength for ITN was greater than for DHITN as shown in Figures 5-17 and 5-18. The absorbance below 400 nm increased sharply from the onset, and the peaks at about 700 and 850 nm increased significantly during the later stages. These results are consistent with the spectra reported by Hillman and coworkers<sup>5</sup> which were obtained during oxidation of ITN at 1.06v, vs. SEC reference electrode. They directly monitored the spectral changes using a transparent ITO electrode. This confirms that the species on the electrode are the same as the species in the solution. Thus, we conclude that when a non-nucleophilic electrolyte (TENBF) is used, the polymer is not formed immediately but that at first the intermediate species predominates and the black powder is only formed later.

With DHITN and ITN the absorption intensity at 540 nm was much weaker than with DMDHITN and DMITN. The absorbance above 600 nm increased very rapidly and the absorption peak at 850nm was even greater than that at 700 nm after 2 hours of the electrooxidation. This confirms that the absorption peaks at 540, 700 and 850 nm respectively are independent and so belong to different intermediate species. Furthermore, compared with the change in spectra of DMITN and DMDHITN, it seems that the species with an absorption peak at 540nm is more active and is rapidly converted to conjugated oligomers with longer chains, such that the absorption intensity of the higher wavelength bands at 700 and 850nm rise sharply.

With increasing reaction time two new absorption peaks at ~ 450 and 480nm are clearly visible. This may result from the reduction of the oxidised species. At the end of the reaction, a blue precipitate was also found in the solution. With DMITN and DMDHITN, under the same conditions, these new peaks were very weak.

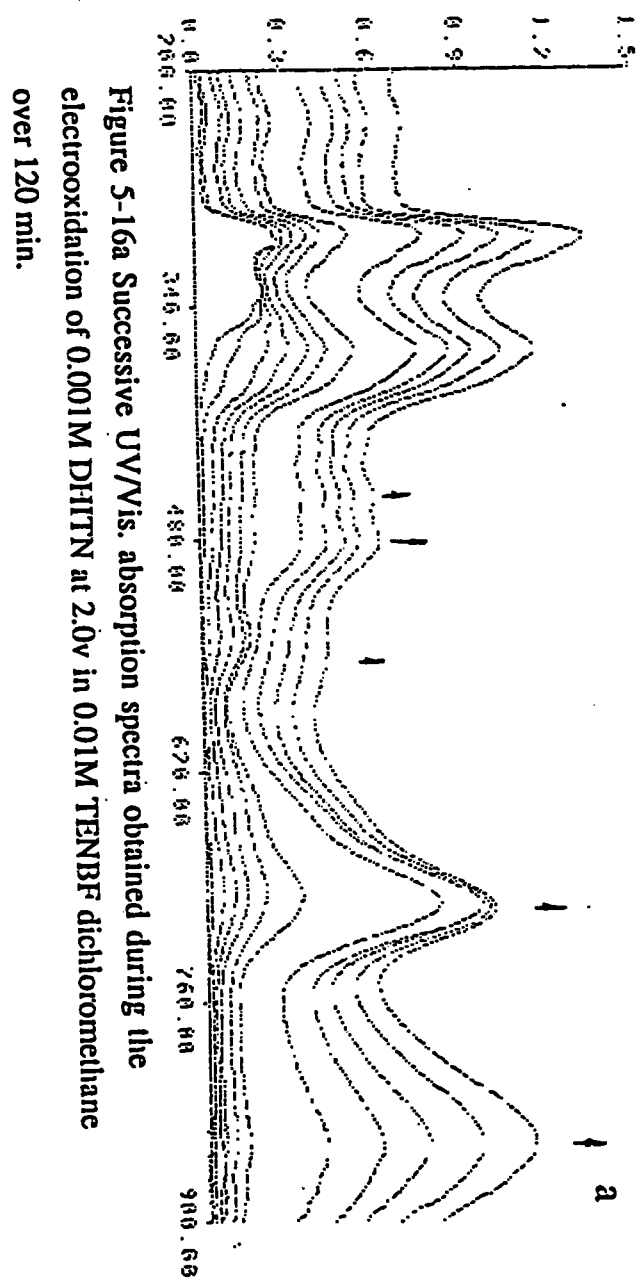


Figure 5-16a Successive UV/Vis. absorption spectra obtained during the electrooxidation of 0.001M DHITN at 2.0v in 0.01M TEBNF dichloromethane over 120 min.

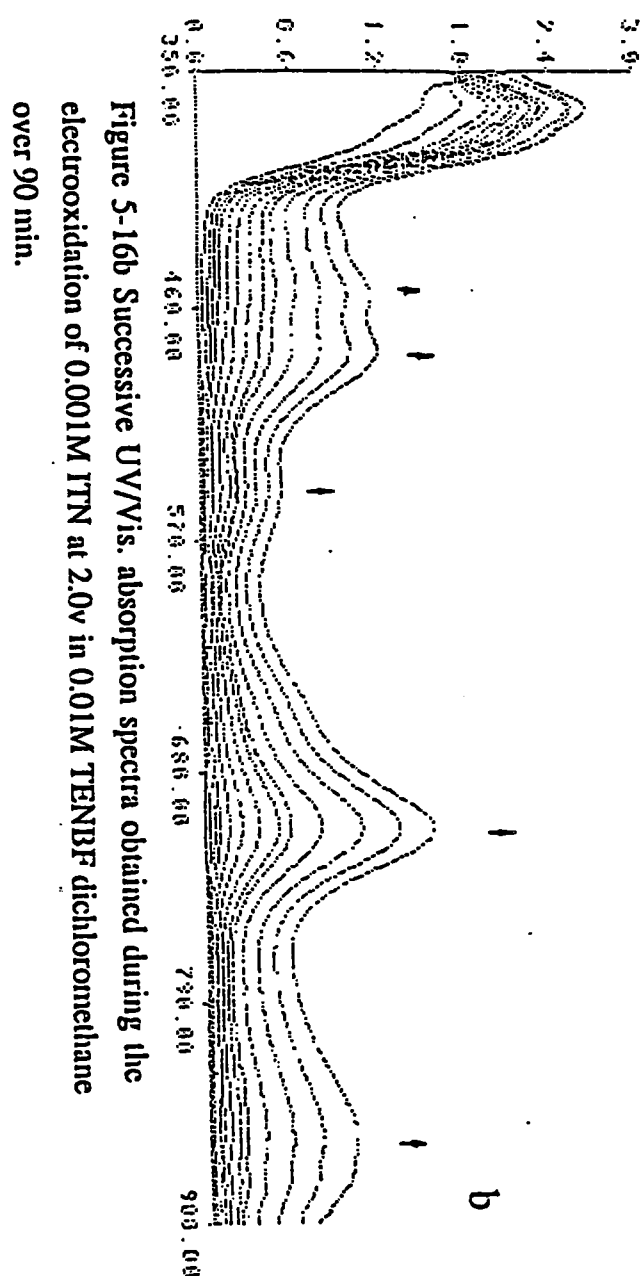


Figure 5-16b Successive UV/Vis. absorption spectra obtained during the electrooxidation of 0.001M ITN at 2.0v in 0.01M TENBF dichloromethane over 90 min.

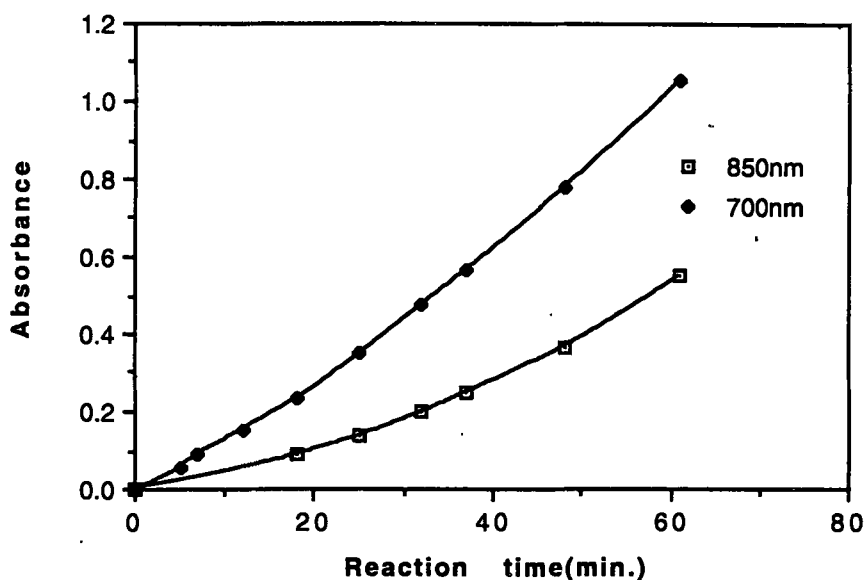


Figure 5-17 Variation of the peak absorption intensity at 700 and 850 nm respectively during the electrooxidation of 0.001M ITN at 2.0v in 0.01M TENBF dichloromethane

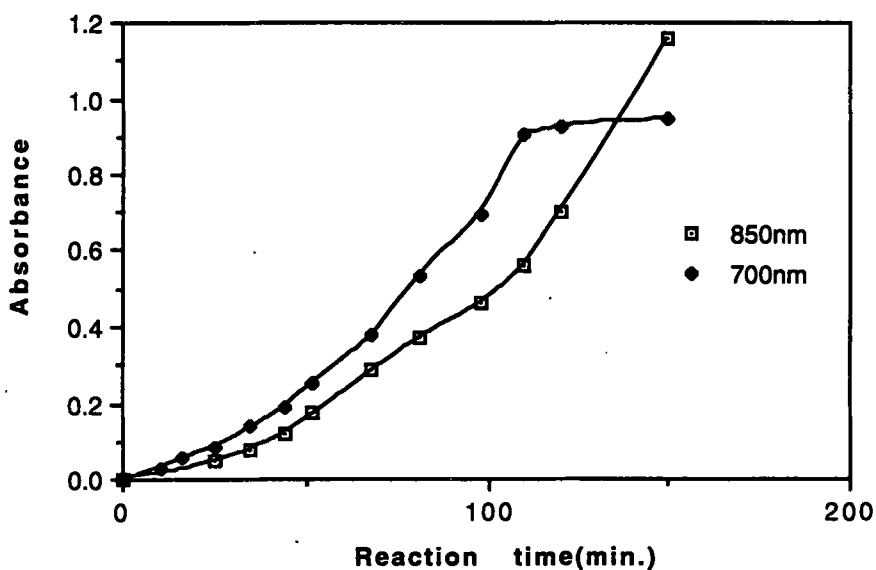


Figure 5-18 Variation of the peak absorption intensity at 700 and 850 nm respectively during the electrooxidation of 0.001M DHITN at 2.0v in 0.01M TENBF dichloromethane

### 3) Effect of TBNBr

Figure 5-19a and b shows successive spectra obtained during the electrooxidation of DMITN and ITN respectively using TBNBr as the electrolyte. As expected, the spectra differed from those in the presence of the non-nucleophilic electrolyte. Even with stirring, polymer films were immediately formed on the electrode accompanied by precipitation of an insoluble powder. The solution was transparent yellow rather than pink or blue. Examination of the spectra of ITN during polymerisation showed that there was only one absorption peak at about 480 nm. This peak could be related to that appearing in the later stages of polymerisation when TENBF was used. When one drop of a reducing agent, diethylamine, was added, the final spectrum did not change. This indicates that no oxidised species were present in the solution. Furthermore, the peaks at 540, 700 and 850 nm did not appear at all during the reaction. This confirms that few, if any, intermediates are formed in solution during the electropolymerisation of ITN in TBNBr.

The spectra obtained with DMITN seem relatively complicated. Although the pink colour could not be seen in the solution a relatively weak absorption at 540 nm was found. In the DMITN system not only was the neutral species observed with a peak at about 480nm, but so were the oxidised species with weak peaks at 540, 700 and 850nm. Unlike when TENBF was used, the absorption peaks at these three wavelengths are very weak, and the intermediates do not build up to any extent. In the early stage of the reaction, the neutral species with a peak at about 480 nm was clearly seen, however, the oxidised species were not observed. It was also noted that an insoluble deposit was immediately formed on the electrode and a precipitate formed in the solution. It seems that using the nucleophilic supporting electrolyte, TBNBr, avoids the formation of a large amount of soluble

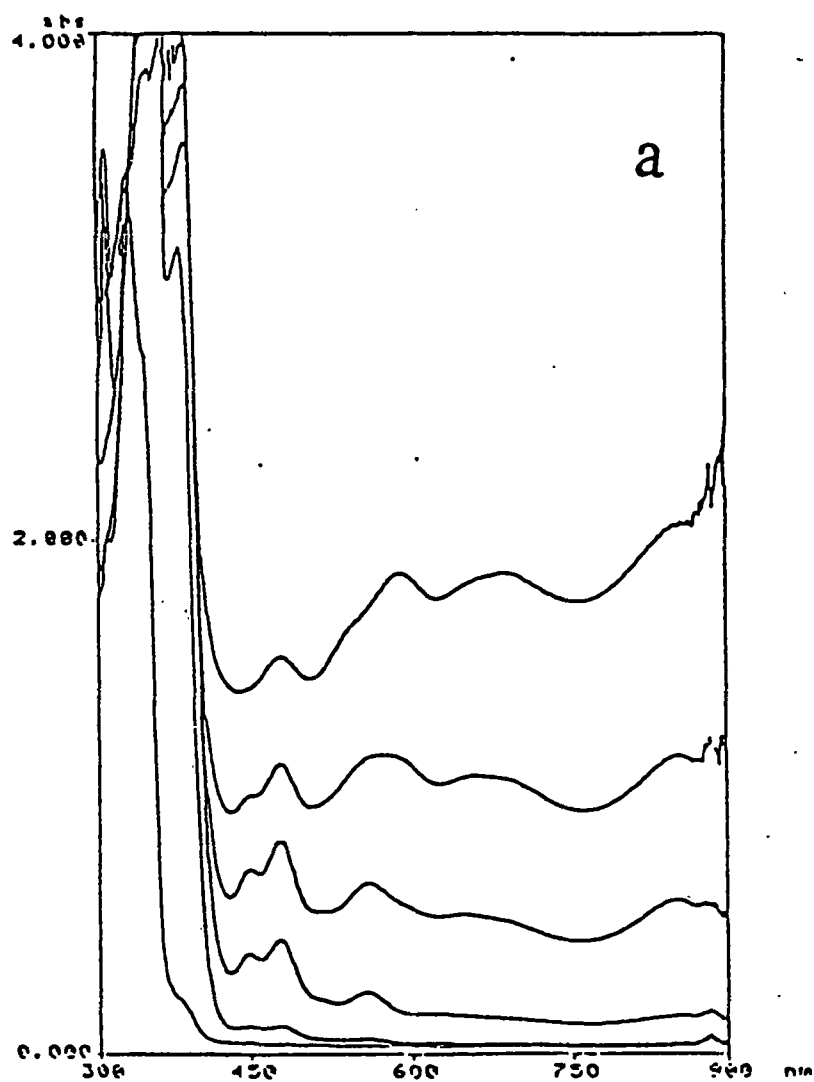


Figure 5-19a Successive UV/Vis. absorption spectra obtained during the electrooxidation of 0.001M DMITN at 2.0v in 0.01M TBNBr dichloromethane (time increasing upwards).

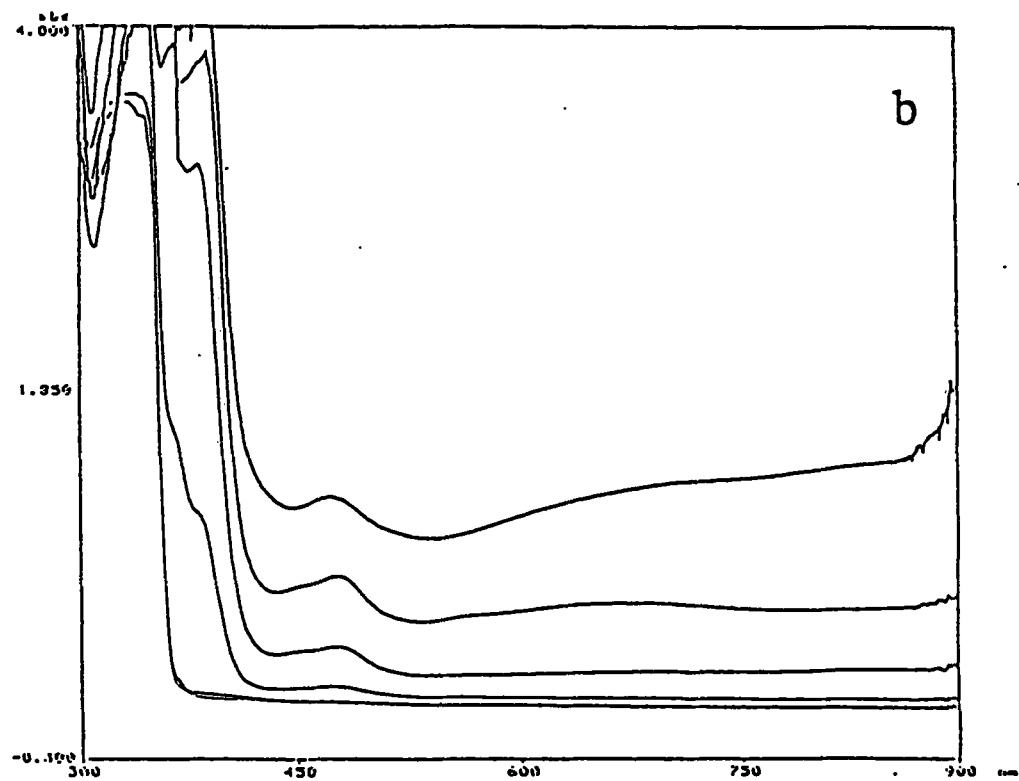


Figure 5-19b Successive UV/Vis. absorption spectra obtained during the electrooxidation of 0.001M ITN at 2.0v in 0.01M TBNBr dichloromethane (time increasing upwards).



intermediate species and promotes conversion of ITN and DMITN to long chain polymers with high conductivity.

#### **4) Effect of Applied potential**

Hillman<sup>5</sup> and Hamnett<sup>22</sup> suggest that when a non-nucleophilic supporting electrolyte is used, a polymer film can only be obtained at a very low applied potential (1.1v vs. SEC). In this work it was found that applying a relatively low potential leads to the formation a polymer with high conductivity. Owing to the relatively weak absorption of the peak at 540 nm when ITN was used, we chose DMITN as the monomer to examine the effect of different potentials on the oxidation process. Figure 5-20 shows successive electron absorption spectra obtained during the electrooxidation of DMITN at 1.4v (a) and 2.4v (b) respectively. Comparison of the diagrams a and b shows that at the higher potential the peak at 540 nm increases very sharply, followed by the peaks at 700 and 850 nm, the peak at 540 nm being the strongest. At the lower potential the three oxidised species with wavelengths at 540, 700 and 850 nm are weaker. The peak at 540 nm has a lower intensity than that at 700 nm and 850 nm. This indicates that the concentration of the short chain oxidised oligomer (possible the dimer of DMITN) remains low during the reaction. Furthermore, at the low potential two extra peaks build up at about 450 and 480 nm, even in the early stages of the oxidation. An insoluble deposit was also found on the working electrode. This is consistent with the results reported by Hillman<sup>5</sup>. However, the presence of intermediate species in solution could not be avoided by only applying a low potential for the polymerisation.

As well as the peaks at 540, 700 and 850 nm associated with the oxidised species, two extra peaks at about 450 and 480 nm could be seen. To identify these species the reaction cell was left in an open circuit after about one hour

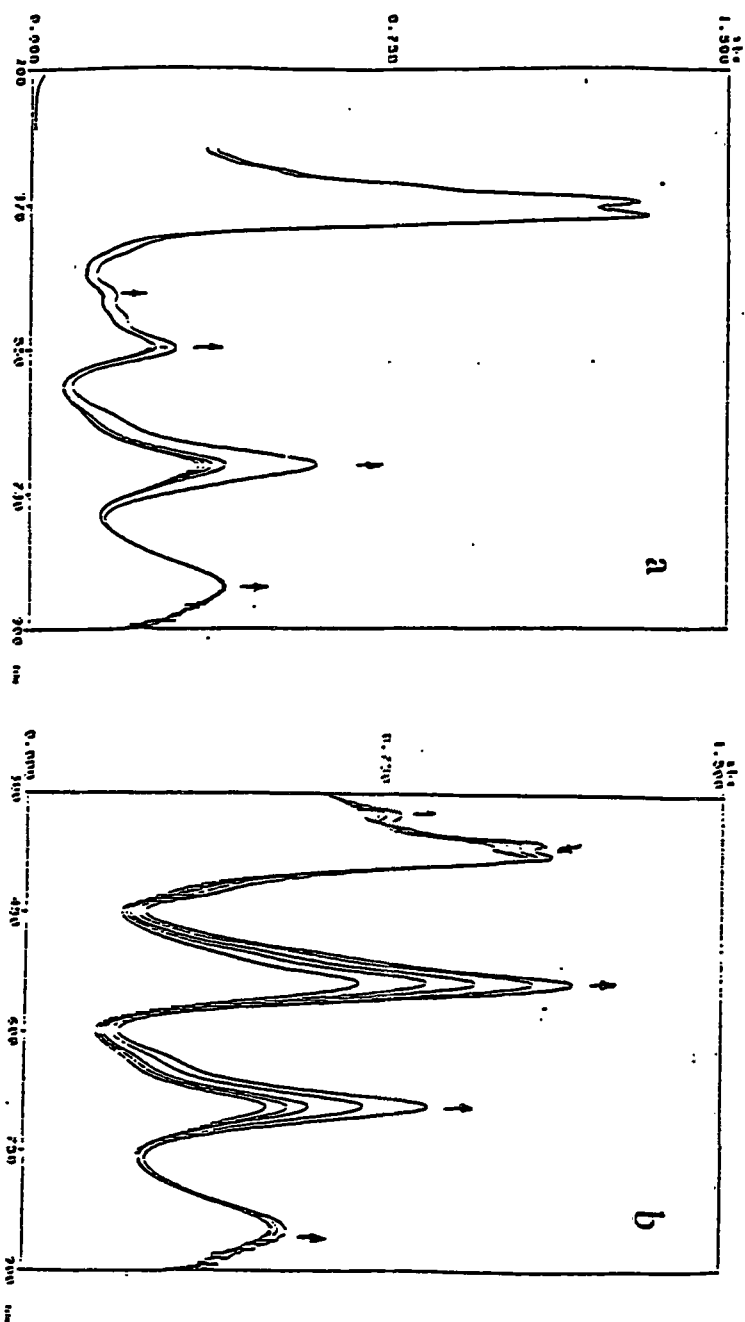
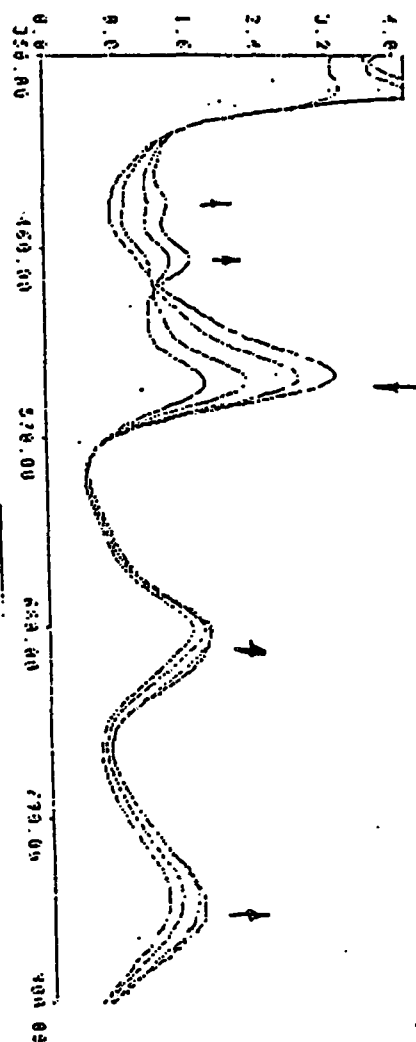


Figure 5-20 Successive UV/Vis. absorption spectra obtained during the electrooxidation of 0.001M DMITN at 1.4V(a) and 2.4V(b) respectively in 0.01M TEBNF dichloromethane (time increasing upwards).

a



b

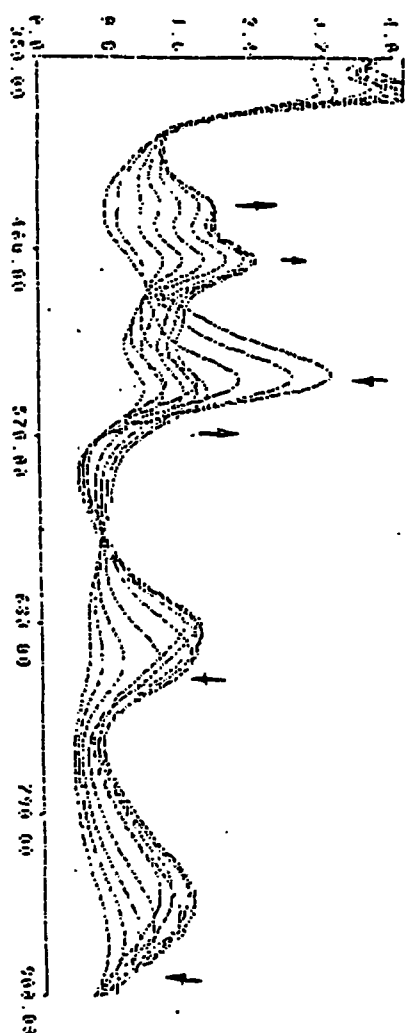


Figure 5-21 Successive UV/Vis. absorption spectra obtained at open circuit after 90 min. electrooxidation of 0.001M DMITN at 2.0v in 0.01M TENBF dichloromethane. a) in 60 min. and b) over 120 min.

of electrooxidation at an applied potential of 2.0v. The absorption spectral change of the sample, which was collected from the reaction cell before the oxidation ceased, was successively recorded at time intervals over a period of two hours as shown in Figure 5-21. At first the peak at 540 nm decreased with two extra peaks at 450 and 480 nm building up. The peak intensities at 700 and 850 nm slightly increased. When the peak at 540nm had nearly disappeared the peaks at 450 and 480 nm levelled off. The peaks at 700 and 850 nm then started to decrease, and other peaks at about 550 nm and a shoulder at about 620 nm built up. At this time some insoluble deposit was formed in the solution. It seems that the species with peaks at 450 and 480 nm may be associated with reaction of the oxidised species (the dimer) which gave rise to peak at 540 nm. The species with a peak at 550 nm and a shoulder at 620nm could be related to further reaction of the oxidised species which gave rise to peaks at 700 nm and 850 nm. It was also noted that when the solution remained for two hours at open circuit the absorption peak at ~ 850nm could still be observed. This indicates that the radical cations of long chain oligomers are very stable.

When a similar experiment was carried out with ITN the peak at 540 nm was very weak and the two absorption at 450 and 480nm gradually built up even during the oxidation at 2.0v, as shown in Figure 5-16(b). When the potential was no longer applied the peak intensities at 700 and 850 nm steadily decreased. A peak at about 550 nm was clearly seen and a shoulder at about 620 nm built up as shown in Figure 5-22. This is very similar to the behaviour of DMITN.

In summary, during the electrooxidation of ITN and DMITN some oxidised species with absorption bands at about 540, 700 and 850nm build up. As the reaction progresses some neutral species with absorption bands at about 450 and 480nm are formed. When the electrolysis is disconnected two new

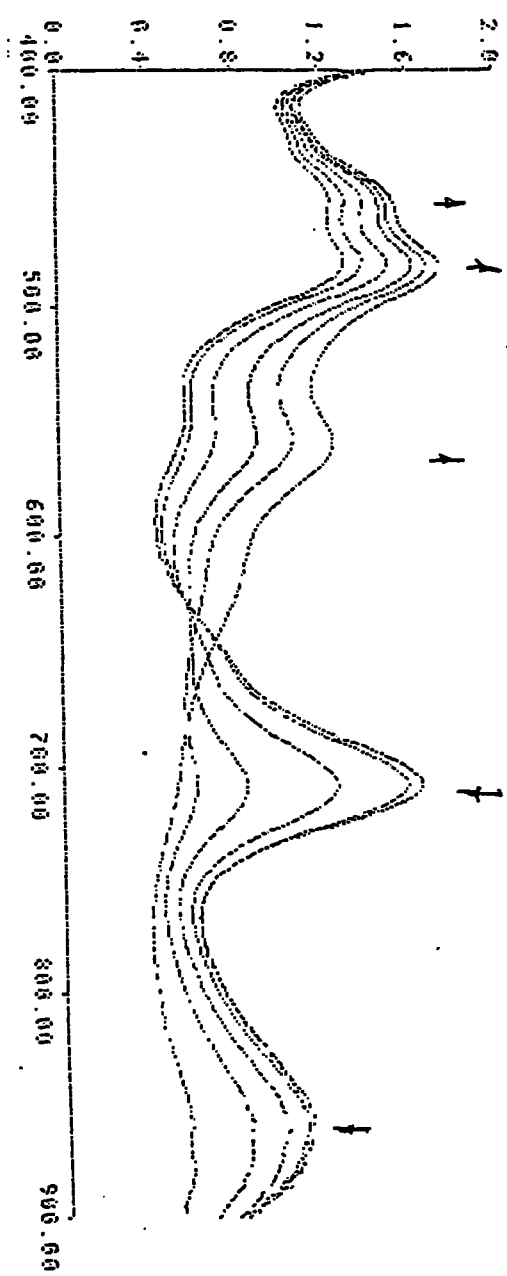


Figure 5-22 Successive UV/Vis. absorption spectra obtained at open circuit after 90 min. electrooxidation of 0.001M ITN at 2.0v in 0.01M TENBF dichloromethane.

species with absorption band at about 550 and 620nm may be formed from coupling, chain transformation and disproportionation of oxidised oligomers in solution.

### **5.3.2 UV/Vis Absorption spectral study of the chemical oxidation of isothianaphthene derivatives**

Although an isothianaphthene polymer(PITN) was produced by both electro and pure chemical oxidations by Wudl<sup>4</sup> ten years ago the mechanism of its oxidation has not been studied. The process is thought to involve a dehydrogenation-coupling process. Such coupling of aromatic nuclei by catalyst-oxidant systems has been extensively reviewed by Kovacic and Jones<sup>23</sup>. The first step is the formation of radical cations, but, the subsequent steps, leading to polymerisation, are still unknown. This mechanism seems to be dependent on the nature of monomers, oxidants and solvents. In this work we examined the change in absorption spectra of isothianaphthenes during chemical oxidation in the presence of ferric chloride( $\text{FeCl}_3$ ) and trifluoroacetic acid( $\text{CF}_3\text{COOH}$ ).

#### **1) DMITN and DMDHITN**

Figures 5-23 and 5-24 show successive spectra of DMITN obtained at fixed time intervals, in the presence of ferric chloride and trifluoroacetic acid. The spectra are identical to those obtained by the electrooxidation of the monomer. The absorption peaks at about 540, 700 and 850nm could be clearly seen. Providing the oxidant was always present, the solution became pink, then green and finally blue. This behaviour is similar to that obtained in the electrochemical process with non-nucleophilic supporting electrolytes. It seems that both reactions follow the same pathway from short chain oligomers to long chain oligomers or polymers.

The long wavelength peak at 850nm increased much more rapidly in the presence of ferric chloride than that in the presence of trifluoroacetic acid. It was found that a black precipitate was formed after two hours of oxidation of the monomer with ferric chloride. However, when the monomer was oxidised with trifluoroacetic acid no precipitate was formed, even after 24 hours the peak at 700 nm still predominated. This indicates that under these circumstances the main product is an oligomer rather than a polymer. This is in agreement with the polymer being partially soluble and having a very low conductivity, when trifluoroacetic acid is used as the oxidant.

In both cases the monomer disappeared quickly when a high concentration of oxidants was added. This suggests that the radical cation of the monomer is easily formed and the rate of polymerisation is not dependent upon the formation of the radical cation of the monomer. Thus, the rate of polymerisation seems to be controlled by the subsequent radical cation coupling processes. In the presence of ferric chloride the radical cations of long chain oligomers could be further coupled to form insoluble long chain polymers with high conductivity. However, in the presence of trifluoroacetic acid the coupling of the radical cations of long chain oligomers may be very slow leading to only disproportionation and chain transformation to form short chain polymers with poor conductivity.

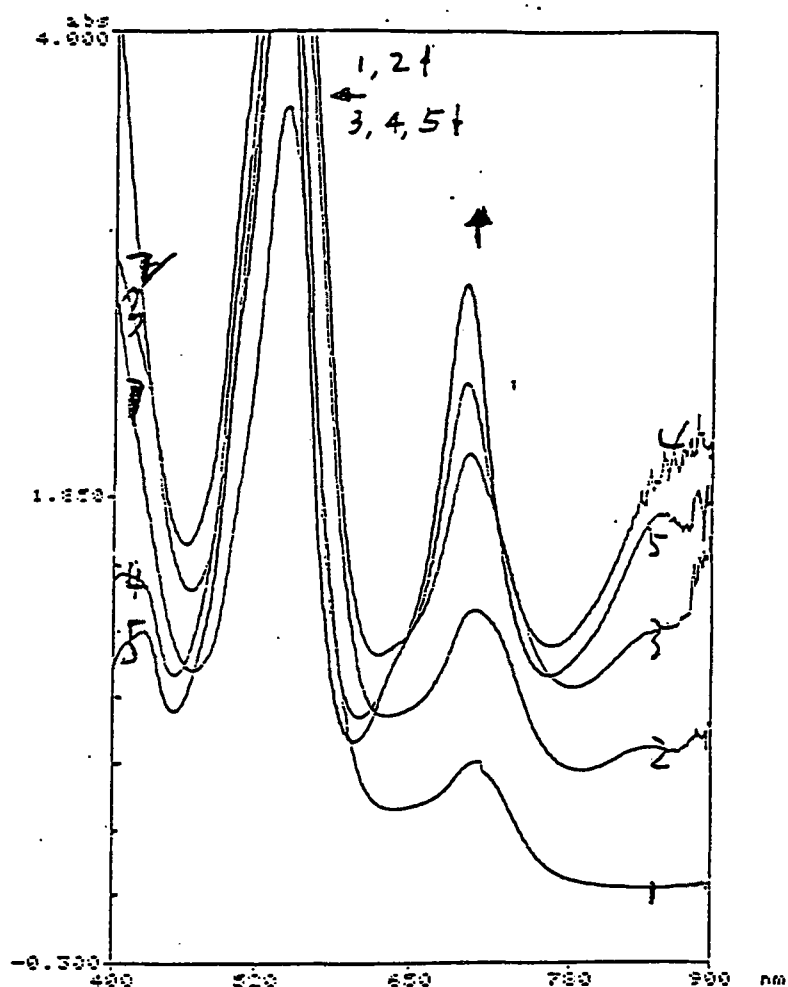
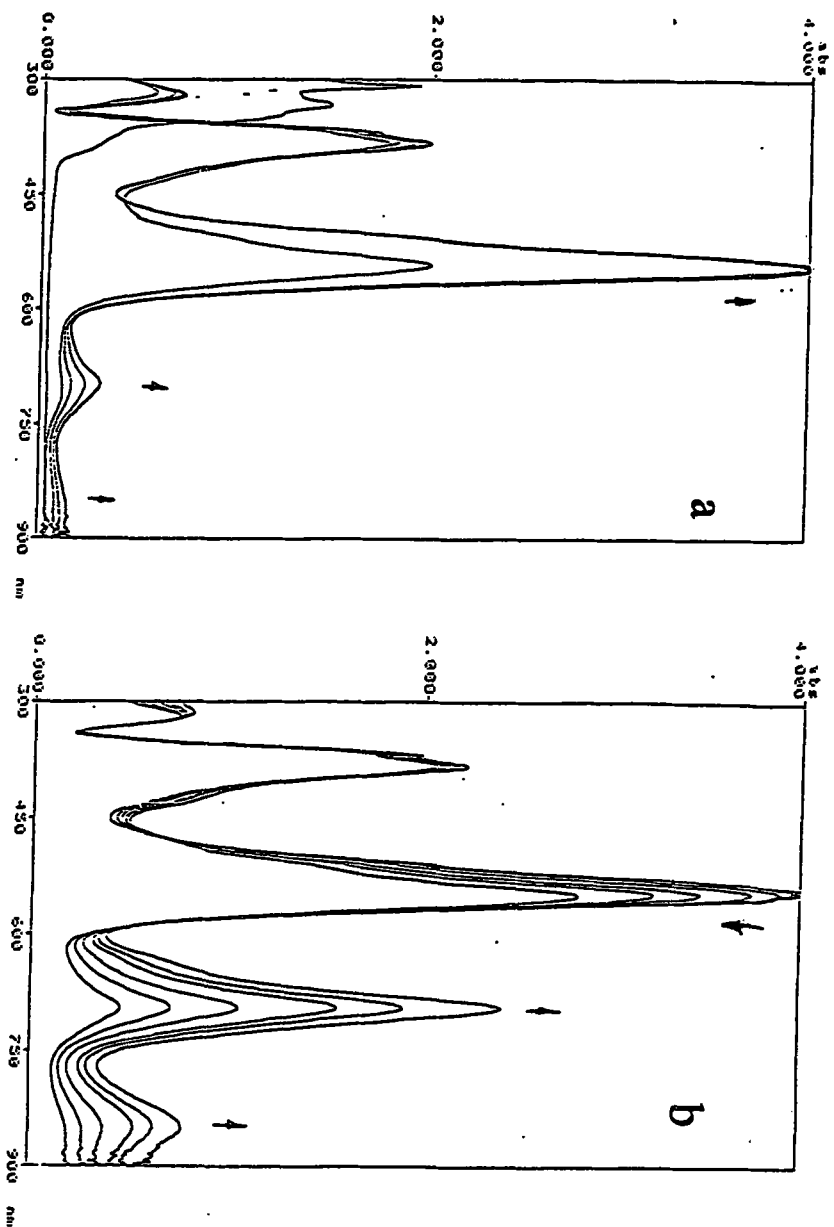


Figure 5-23 Successive UV/Vis. absorption spectra obtained during the chemical oxidation of 0.002M DMITN in dichloromethane with 0.02M ferric chloride in 2 hours. Curves 1, 2, 3, 4 and 5 were obtained after 10, 20, 60, 90 and 120 min. respectively.





**Figure 5-24** Successive UV/Vis. absorption spectra obtained during the chemical oxidation of 0.002M DMITN in dichloromethane in the presence of 0.02M trifluoroacetic acid with the time increasing in 3 hour intervals (a+b).

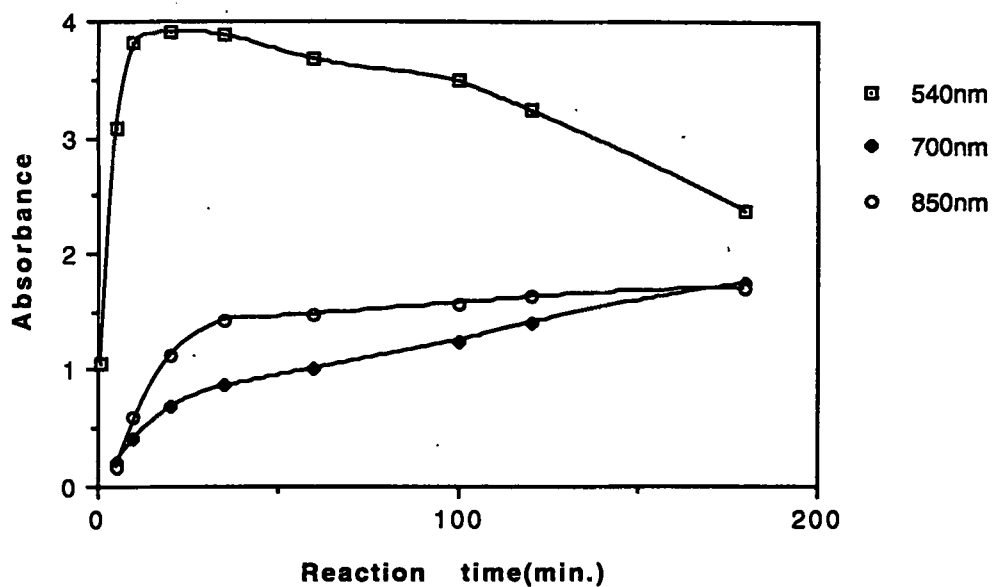


Figure 5-25a Variation of the peak absorption intensity at 540, 700 and 850 nm respectively during the chemical oxidation of 0.002M DMITN with 0.04M trifluoroacetic acid in dichloromethane

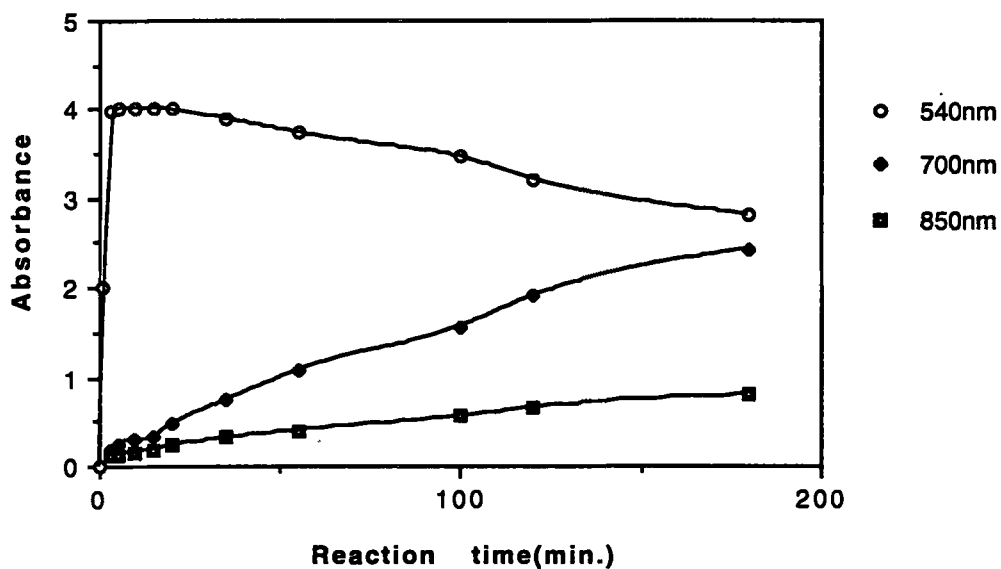


Figure 5-25b Variation of the peak absorption intensity at 540, 700 and 850 nm respectively during the chemical oxidation of 0.002M DMITN with 0.02M trifluoroacetic acid in dichloromethane

When the concentration of trifluoroacetic acid was doubled no precipitate was formed after 24 hours, the only difference was that, as shown in Figure 5-25 a and b, the peak intensity at 850 nm increased more rapidly in the presence of 0.04M trifluoroacetic acid than in the presence of 0.02M trifluoroacetic acid. The peak intensity at 850 nm was higher than that at 700 nm for most of the reaction. However, after an initial burst the absorption intensity at 850 nm only rose very slowly and eventually levelled off. Conversely, the peak at 700 nm steadily increased and eventually exceeded the peak at 850 nm. At a low concentration of the oxidant(0.02M), the peak intensity at 700 nm increased much more rapidly than that at 850nm throughout the reaction. This indicates that the higher the trifluoroacetic acid concentration, the greater the chance that a relatively long chain oligomer will be obtained.

To determine whether the three main peaks at 540, 700 and 850nm belong to the neutral or oxidised intermediate species, a reducing agent, diethylamine, was added. Figure 5-26a shows the spectral change, on addition of one drop of trifluoroacetic acid to 0.001M of DMITN in dichloromethane. The spectrum of the solution was recorded within two minutes of the addition. The absorption peaks of the monomer at 334, 308, 295 and 282 nm disappeared and two strong peaks at about 380 and 540 nm developed. When two drops of diethylamine were added the peak at 540 nm quickly disappeared but the peak at 380nm remained, and a shoulder at about 480 nm was apparent. This confirms that the peak at 540nm is related to an oxidised intermediate species. Guay and coworkers<sup>18</sup> have shown that the radical cations of thiophene oligomers (trimer, tetramer and pentamer) have absorption peaks at 574, 666 and 743 nm respectively. This may give an indication that the oxidised species with an absorption peak at 540nm might be a radical cation of the DMITN dimer. It seems that the monomer is

rapidly coupled to form a dimer and further oxidised to a radical cation when the oxidant is introduced. However, the further coupling to give a long chain polymer takes a longer time.

Figure 5-26b shows the spectral change of DMITN at set time intervals, when two drops of trifluoroacetic acid were added and the reaction left for one hour, then reduced with 3 drops of diethylamine. The final bold curve shows that the peaks at 540, 700 and 850 nm immediately disappear as soon as the reducing agent was added. The colour of the solution changed from green-blue to purple. Furthermore, two pairs of absorption peaks developed at 450 and 480 nm and 510 and 550 nm. It seems that these peaks are associated with reduction of the oxidised species.

Mass spectral analysis(EI) was used to examine the reaction residues in each case. When the oxidation of DMITN was terminated with the reducing agent, within two minutes, only the dimer and monomer fragments with peaks at 162(100) and 322(38.0) were observed. When the oxidation was terminated after one hour, fragments of trimer, tetramer and pentamer were observed at 482(14.3), 642(1.0) and 802(0.1) respectively, together with fragments of the monomer and dimer, as shown in Figure 5-27. This confirms the formation of long conjugated oligomers. Some oligomers include five or more isothianaphthene units.

When the 1,3-dihydro compound, DMDHITN, was oxidised the successive spectra were similar to those obtained using DMITN. With the 1,3-dihydro compound the reaction rate was much slower than that with the fully aromatic monomer. After 30 hours of oxidation with trifluoroacetic acid, the absorption peak at 540 nm was still very strong and did not decrease, as shown in Figure 5-28. No precipitate was observed.

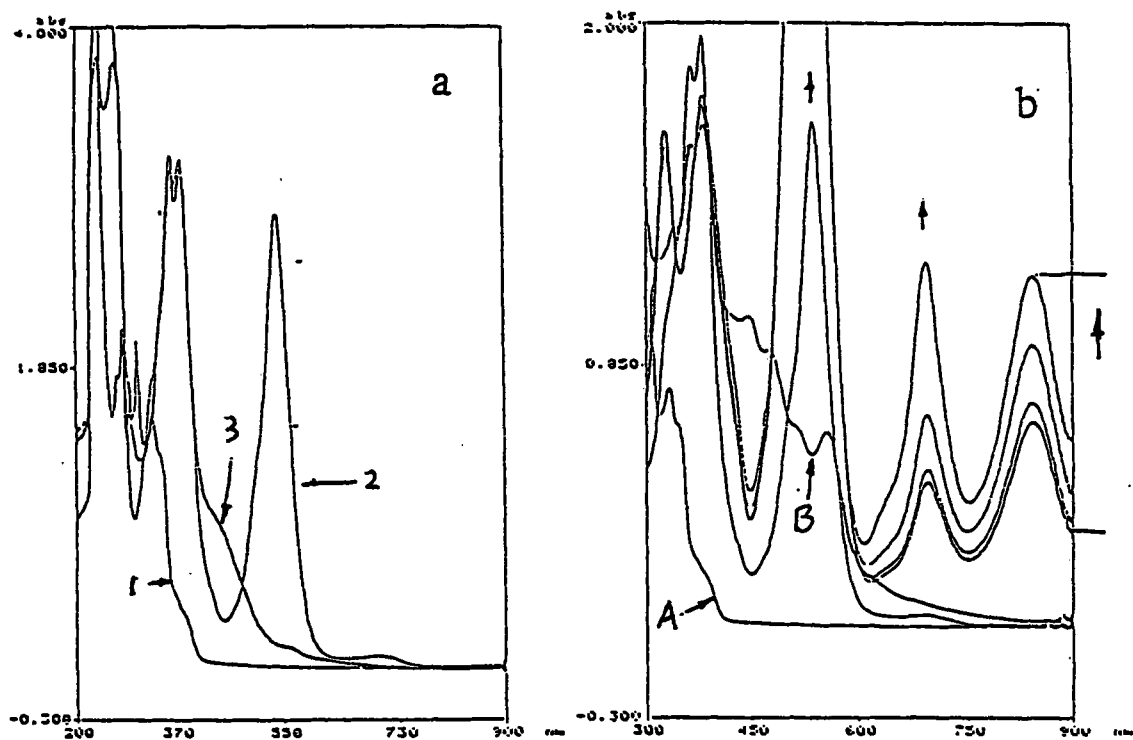


Figure 5-26 UV/Vis. absorption spectra for the chemical oxidation and reduction of 0.0005M DMITN with trifluoroacetic acid and diethylamine respectively in 2 ml of dichloromethane. a): recorded in 0 min.(Curve 1) and 2 min.(Curve 2) after one drop of trifluoroacetic acid was added, followed by adding two drops of diethylamine(Curve 3). b): recorded successively after two drops of trifluoroacetic acid were added in one hour, followed by adding four drops of diethylamine(Curve A and B were recorded before the oxidation and after the reduction respectively).

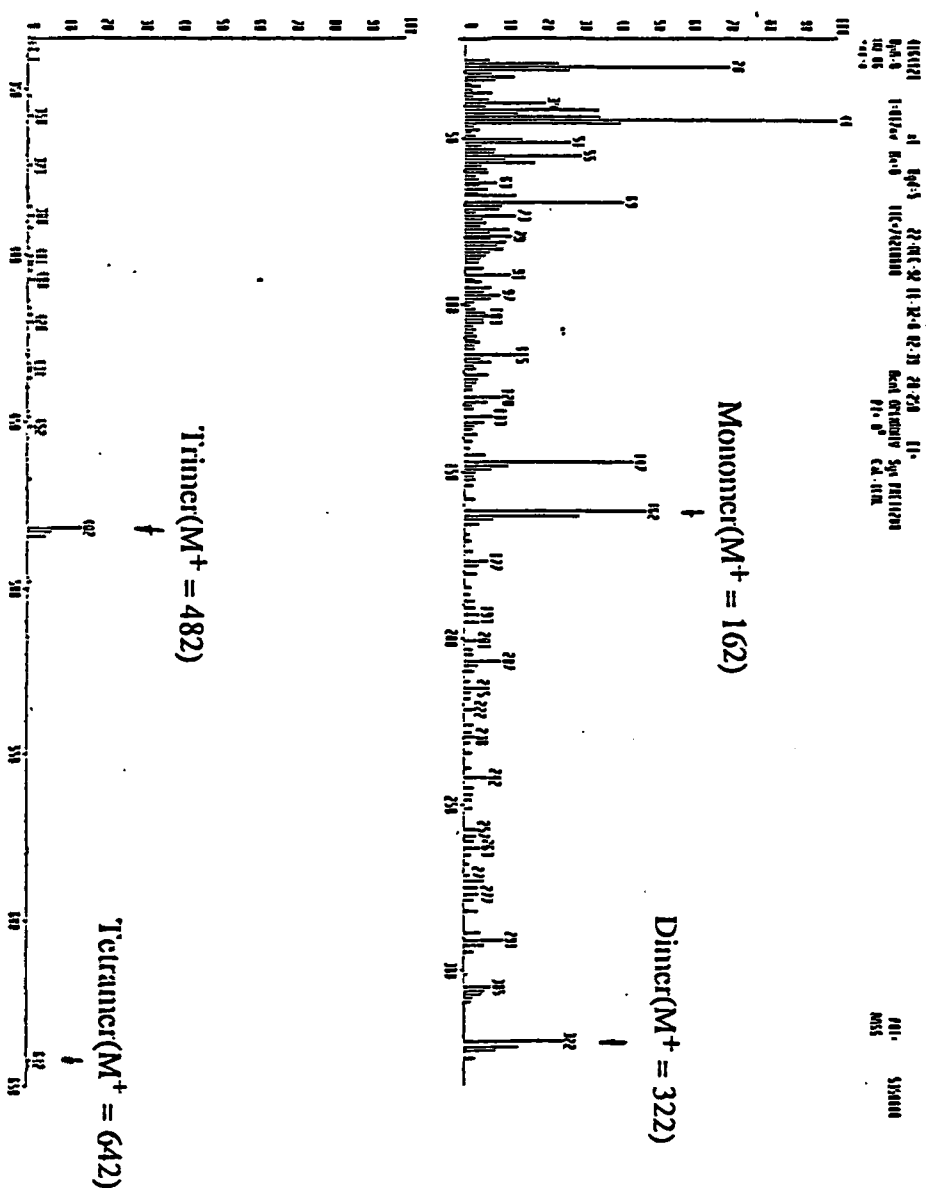
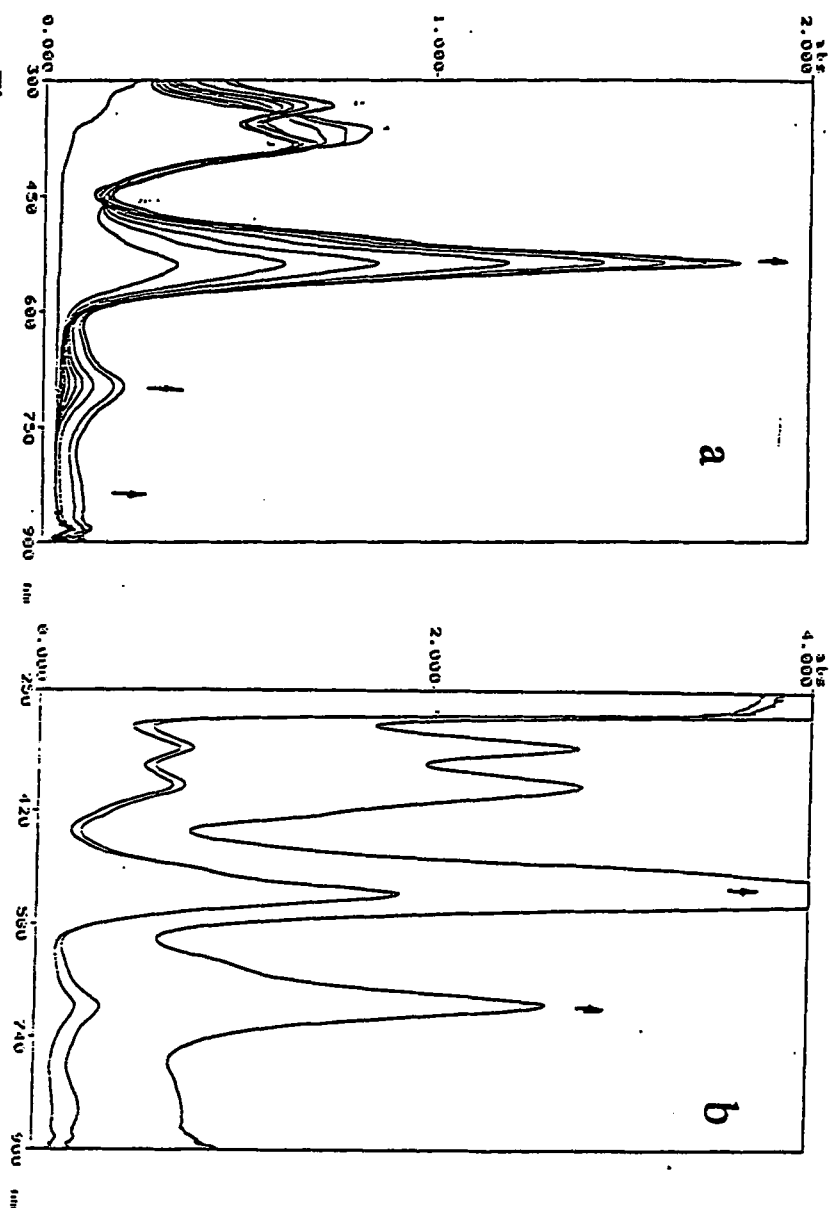


Figure 5-27 Mass spectrum of oxidised DMTN with trifluoroacetic acid in dichloromethane.



**Figure 5-28** Successive UV/Vis. absorption spectra obtained during the chemical oxidation of 0.002M DMDHTN in dichloromethane in the presence of 0.02M trifluoroacetic acid. a) in 9 hours and b) from 9 to 30 hours.

## 2) ITN and DHITN

Figures 5-29 and 5-30 show successive spectra of ITN in the presence of ferric chloride and trifluoroacetic acid respectively at set time intervals. As with DMITN system, three absorption peaks at 540, 700 and 850 nm built up after addition of the oxidants. When ferric chloride was used as an oxidising agent the peak intensity at 850nm increased very sharply and precipitate started to form after two hours. In the presence of trifluoroacetic acid no precipitate formed even after 12 hours. Figure 5-30 shows that the peak intensity at 540 nm first increased then decreased rapidly over the three hour period, and peaks at 450, 480 and 550 nm developed. However, when ferric chloride was used the three peaks at 540, 700 and 850 nm increased continually during the two hour period, as shown in Figure 5-29. It seems that in the presence of trifluoroacetic acid the oxidised dimer species couples and deprotonates to form a neutral species. This could be oxidised again or remain in the neutral state, since some of the new peaks which developed had the same absorption wavelength as the neutral species obtained after reduction (see Figure 5-22).

To examine the spectral change of ITN over a long reaction time a dilute solution of ITN(0.0005M) with 0.05M of trifluoroacetic acid was left for 3 days and the spectrum recorded at intervals of 0, 2minutes, 1 day, 3 days and after complete reduction with diethylamine. The results are shown in Figure 5-31a. During the final stages the solution was green-blue and turned deep purple after reduction. The peaks at 700 and 850 nm disappeared as soon as diethylamine was added. The absorption intensity over the range 400 to 600 nm increased sharply. This is indicative of the formation of neutral oligomers from the oxidised species associated with the peaks at 700 and 850 nm. It was also observed that after reduction an absorption shoulder developed at about 600 ~ 650nm. In the reaction cell there was a fine blue



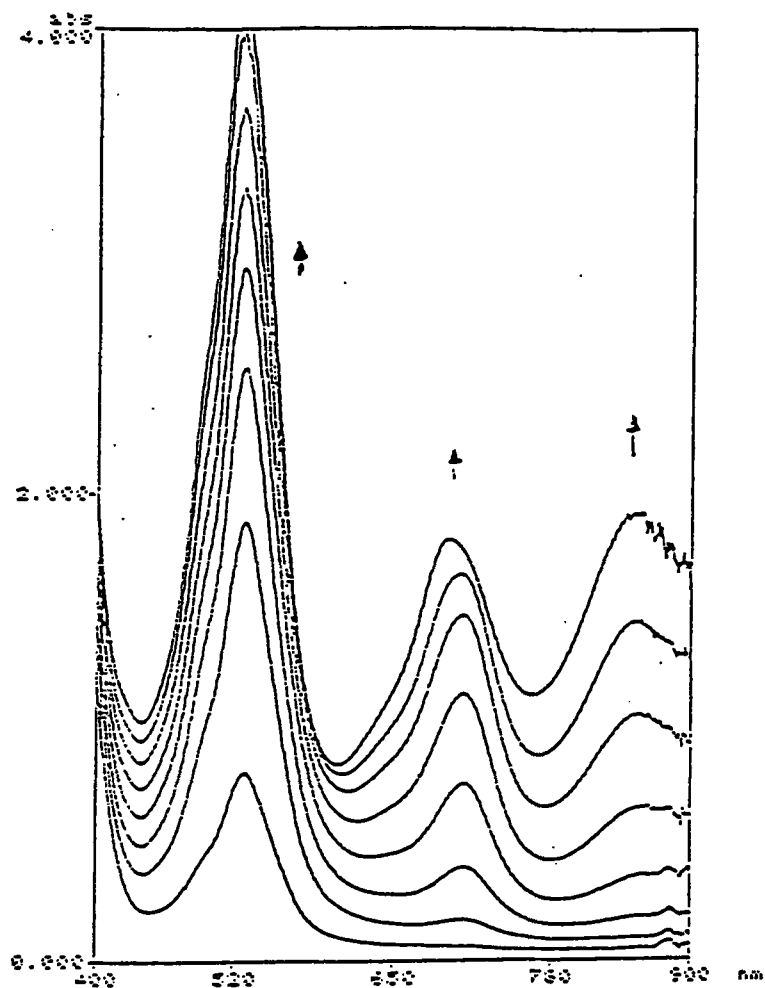
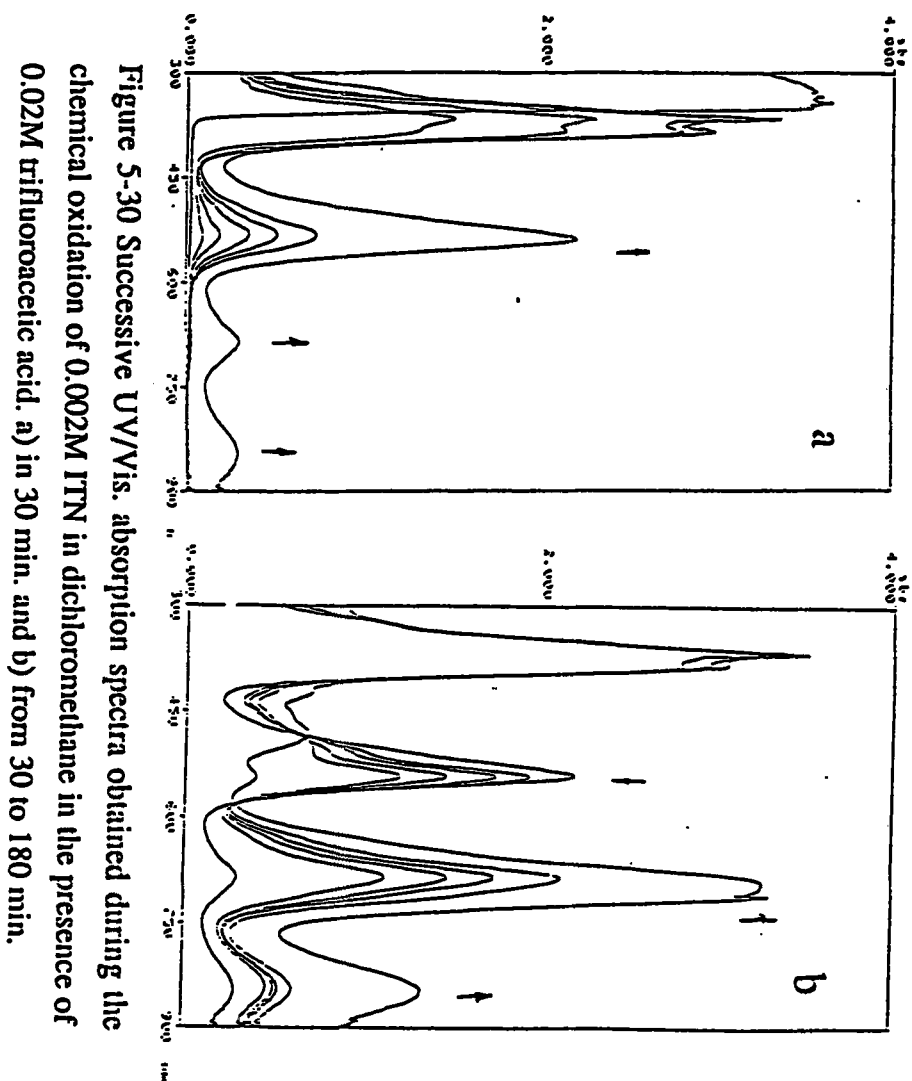


Figure 5-29 Successive UV/Vis. absorption spectra obtained during the chemical oxidation of 0.002M ITN in dichloromethane in the presence of 0.02M ferric chloride over two hours.



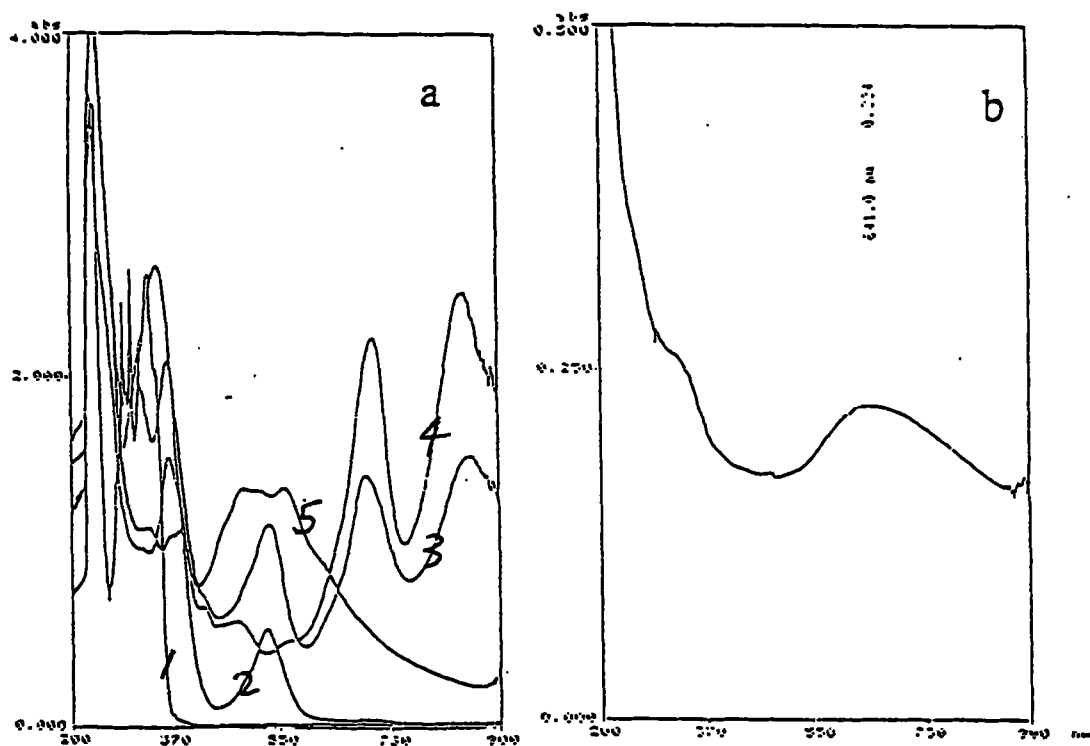


Figure 5-31 Comparison of the UV/Vis. absorption spectra for the chemical oxidation and reduction of 0.0005M ITN with trifluoroacetic acid and diethylamine respectively in 2 ml of dichloromethane. a): recorded at 0 min.(Curve 1), 2 min. (Curve 2), 1 day(Curve 3), 3 days(Curve 4) after one drop of trifluoroacetic acid was added, and after reduction by adding two drops of diethylamine(Curve 5). b): the spectrum of a blue film directly deposited on the surface of the UV cell over three day oxidation.

film deposited on the surface of the cell. The film had an absorption peak at 641 nm, as shown in Figure 5-31b. It seems a polymer may be formed which is only partially soluble in dichloromethane. Nevertheless, soluble oligomers still predominate in the system. Investigating the residue using Mass spectroscopy(EI) showed the presence of oligomers with fragment peaks at 134(100), 266(46.4), 398(16) and 530(0.7) corresponding to the monomer, dimer, trimer and tetramer respectively.

When the 1,3-dihydro compound DHITN was oxidised with ferric chloride and trifluoroacetic acid, the successive spectra of DHITN were quite different from those of other monomers, as shown in Figure 5-32. The three peaks at about 540, 700 and 850 nm were weak. Two strong peaks at about 480 and 640nm could be seen early in the reaction. After reduction with diethylamine the two peaks at 480 and 640 nm disappeared together with the peaks at 540, 700 and 850 nm leading to two flat shoulders at about 450 and 560 nm.

### **3) MeODHITN and its polymer**

During electrooxidation of both MeODHITN or MeOITN an electroactive polymer was immediately deposited on the electrode. The resulting polymer is blue in the oxidised state and brown in the neutral state. The polymer in the oxidised state is partially soluble in dichloromethane. The absorption spectrum of the dissolved polymer from the working electrode, in dichloromethane, showed two absorption peaks at about 590 and 750 nm. There were no other absorption peaks above 400 nm.

The polymer made from MeODHITN by electrolysis has a brown colour in the neutral state. This not only undergoes reversible electrochemical reaction but also reversible chemical oxidation, as shown in Figure 3-22(in page 126) When trifluoroacetic acid was added to the polymer solution, the

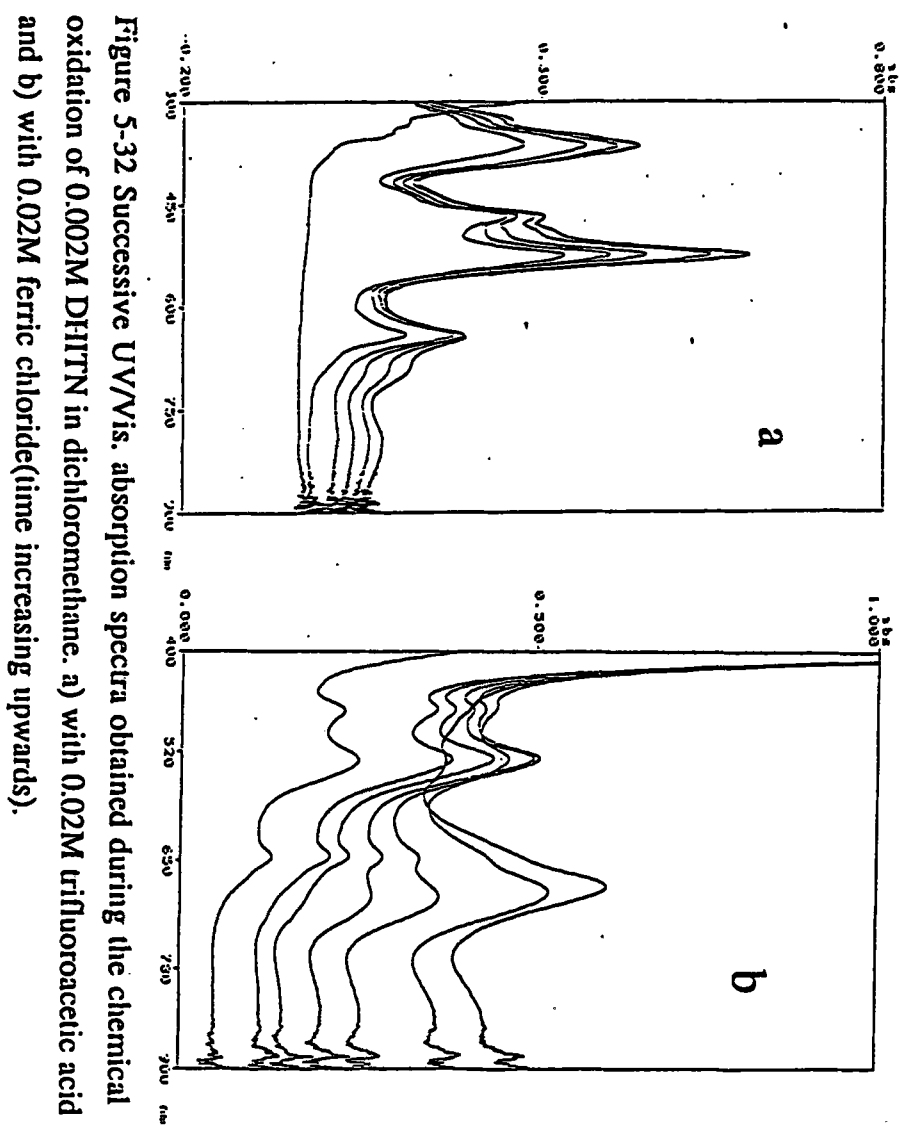


Figure 5-32 Successive UV/Vis. absorption spectra obtained during the chemical oxidation of 0.002M DHITN in dichloromethane. a) with 0.02M trifluoroacetic acid and b) with 0.02M ferric chloride (time increasing upwards).

absorption shoulder at about 450 nm immediately disappeared and two peaks at 590 and 750 nm developed. When a reducing agent, diethylamine, was added, the spectrum of the oxidised polymer promptly reverted to that of the original neutral form. This indicates that chemical oxidation does not irreversibly change the structure of the polymer.

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# Chapter Six

## Conclusions and Recommendation for Further Work

### 6.1 Conclusions

1) A range of isothianaphthene derivatives have been prepared including DHITN, ITN, DMDHITN, DMITN, MeODHITN, MeOITN, PhITN and thiophthalide. Silicon containing compounds including TPSCP, TMSCP and TMSCPD have also been successfully synthesised in good yields. To prepare functionlised silole derivatives we have prepared 1,1,4,4-tetrachlorobutadiene and a rigid *cis* tetrachlorobutadiene( $\alpha,\alpha'$ -tetrachloromethlenecyclopentane).

2) A new electroactive polymer, poly(5,6-dimethylisothianaphthene) (PDMITN), was prepared by electrochemical and chemical oxidation of either 5,6-dimethylisothianaphthene(DMITN) or 5,6-dimethyl-1,3-dihydroisothianaphthene(DMDHITN). The nature of the supporting electrolyte and solvent dramatically affected the conductivity of the polymer formed by the electrochemical route. Using a nucleophilic electrolyte(TBNBr) and dichloromethane a long chain polymer could be obtained from DMITN with a high conductivity, up to  $100 \text{ Scm}^{-1}$ . The polymer has an electronic absorption maximum at 830 nm and offset of the absorption band (the  $\pi\text{-}\pi^*$  transition band) is at about 1.1ev. Thus, the band gap of PDMITN is the same as that of PITN, 1.1ev. The presence of methyl groups on positions 5 and 6 of the isothianaphthene ring does not affect the band gap. For both PITN and PDMITN a significant colour change from blue or green-blue (neutral state) to slightly yellow-transparent (oxidised state) could be found with cyclic volammetry. However, the introduction of two methyl groups reduced the oxidation peak of DMITN to 1.26v



compared with that of ITN, 1.35v. The substituents also stabilised the oxidation state of the polymer. It could be scanned to 1.3v until it degraded, compared to 1.1v for PITN.

When TBNBr was replaced by a non-nucleophilic electrolyte(TENBF) a pink coloured species, followed by green and blue coloured species, were formed successively on the electrode or in the solution. The resulting polymer(powder) had a poor conductivity of about  $10^{-3} \text{ Scm}^{-1}$ .

3) We have also made a novel electroactive polymer, poly(4-methoxyisothianaphthene)(PMeOITN), from both 4-methoxyisothianaphthene(MeOITN) and 4-methoxyl-1,3-dihydroisothianaphthene(MeODHITN) by electro-oxidation in the presence of a non-nucleophilic supporting electrolyte(TENBF) in acetonitrile. When a nucleophilic supporting electrolyte(TBNBr) was used no polymer was formed but the monomer disappeared. A methoxy group in position 4 of the isothianaphthene ring was found to dramatically affect the conductivity of the polyisothianaphthene. Its conductivity is below  $10^{-5} \text{ Scm}^{-1}$ . However, the resulting polymer is very soluble in dichloromethane and chloroform. The polymer is brown in the neutral state and green-blue in the oxidised state.

Oxidation of a film of PMeOITN is electrochemically reversible. The oxidation and reduction peaks are at 0.8v and 0.4v respectively. However, the cyclic voltammograms of the polymer film are not very stable. The electronic absorption spectrum of the polymer in dichloromethane shows that when the polymer is in the neutral state there is an absorption peak maximum at 393 nm and shoulder at 450 nm. The offset of the absorption band (the  $\pi-\pi^*$  transition band) is at about 700 nm(1.8ev). Thus, the polymer exhibits a band gap of about 1.8ev which is much higher than that of PITN. After the polymer has been oxidised with ferric chloride or

trifluoroacetic acid, two longer wavelength peaks at 595 and 760 nm build up and the shoulder at 450 nm disappears. When diethylamine is added the UV/Vis spectrum reverts to that of the original reduced form.

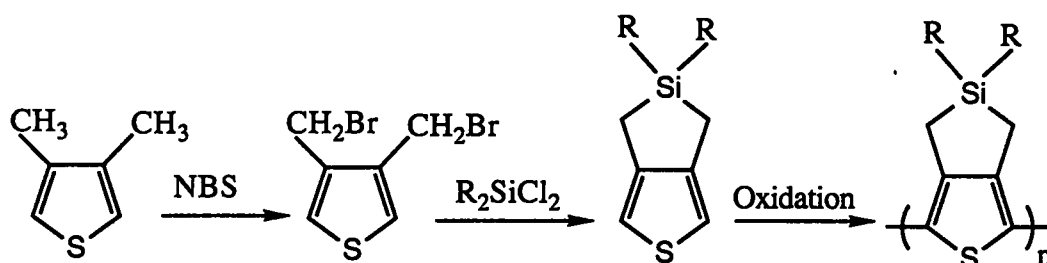
4) From HPLC and UV/Vis spectral studies the rates of the consumption of ITN, DMITN and MeOITN monomer are very high during both electrochemical and pure chemical oxidation. However, the rates of consumption of DHITN, DMDHITN and MeODHITN monomers are very slow.

5) The mechanism of electrochemical oxidation of ITN and DMITN in the presence of a non-nucleophilic electrolyte such as TENBF, which is similar to that of the pure chemical oxidation, is most likely a radical cation coupling mechanism (step growth polymerisation) from dimer, oligomer to polymer. The coupling process is much slower than that of the parent thiophene as a result of the aromatic benzene rings which stabilise the radical cation and thus reduces its activity. This explains why we can observe the optical absorption of the intermediate products during the polymerisation. It is the large amounts of radical cations and neutral species of the intermediates in solution that give rise to the formation of powder products with short chain length and the defects in the polymer by chain disproportionation, transformation and other side-reactions in solution.

## **6.2 Recommendation for Further Work**

1) Although a number of silicon containing cyclic compounds have been successfully prepared, the required polysiloles were not made in this work. Thus, it is necessary to find alternative ways of preparing such materials such as using rigid *cis* tetrachlorobutadienes, which could cyclise with dichlorosilanes to form silacyclopentadienes functionalised with chlorine groups. These compounds may be polymerised using Grignard agents in the

presence of nickel complexes. A second future objective could be the preparation of compounds containing both silicon and sulphur atoms as monomers for polymerisation. An outline of a possible procedure is shown below.



2) In this work the nature of the supporting electrolyte dramatically affects the electrochemical polymerisation of ITN, DMITN and MeOITN. When a nucleophilic electrolyte(TBNBr) was used ITN and DMITN could be converted into high conducting polymers, however, MeOITN could not be converted into a polymer but gave only soluble by-products. The important role played by the electrolyte in the reaction is not known. In future work the soluble by-products obtained with MeOITN need to be isolated and identified. We will then know whether the electrolyte reacts directly with the monomer or intermediates.

3) In the presence of a non-nucleophilic supporting electrolyte(TENBF), ITN and DMITN were first converted into soluble intermediate species(oligomers) and then to polymers with poor conductivity. To identify these species HPLC-Mass spectrometry needs to be used for monitoring the formation of the intermediates during the reaction. Thus we can find out which species predominate in the reaction at different stages. We have tried to use HPLC-Mass spectrometry courtesy of Hoechst Ltd. Unfortunately, owing to instrumental problem, no results have been obtained.

4) We also found that using a mixture of PhITN and ITN leads to the formation of a polymer with high conductivity. This polymer needs to be

further characterised using solid state NMR and other techniques to determine whether the polymer is a copolymer of PhITN and ITN or a homopolymer of ITN.

5) In this work two ill-defined oxidation peaks were found for PDMITN during cyclic voltammetry, which may be attributed to the formation of polarons (spin species) and bipolaron (spinless species). To confirm this suggestion the ESR spectrum needs to be measured using in situ electrochemical methods. This technique has recently contributed much to the understanding of the simple polythiophene.

# Chapter Seven

## Experimental Methods

### 7.1 Materials

#### 7.1.1 Materials used for the synthesis of monomers

$\alpha,\alpha'$ -Dibromo-o-xylene, 96% was supplied from Aldrich Chemical Company Ltd. and recrystallised from petroleum ether 40-60°C.

Thiodiglycolic acid; Chlorotrimethylsilane; Iodotrimethylsilane; Dichlorodimethylsilane; 2,3-Dimethylbutadiene; Pyridine; Triethylamine; Diethylamine; Phenylisocyanate; Diphenyldichlorosilane; and Ethane-1,2-diol were purchased from Aldrich Chemical Company Ltd. and distilled before used.

Sodium sulfide nonahydrate, 98%, A. C. S reagent; Sodium periodate, 99.8 + %, A. C. S reagent; Aluminum oxide, activated, neutral, Brockmann I, standard grade; Paraformaldehyde, 95%; o-Xylene, 98%; Hydrochloric acid, 37%, A. C. S reagent; 3,4-Dimethylanisole; 2,3-Dimethylanisole; N - Bromosuccinimide, 99%; Benzoyl peroxide, 97%; o-Tolunitrile; Thiourea; Potassium *tert* - butoxide, 95%; Sodium hydride, dry, 97%; Phenanthrenequinone, 80%; Sodium, spheres, 3 to 8 mm in odorless mineral spirits; Veratrole; 1, 2 - Naphthoquinone; Tetrachloro-benzoquinone; Diphenyl acetylene; Lithium, wire, 99.9%, in mineral oil; Methyl-2-butynoate; Bromine, 99.5%; 3-Chloroperoxybenzoic acid, 50 - 60%; Magnesium monoperoxyphthalate; Butyllithium, 2.5M in hexane; Magnesium turnings, 98%; Hexachlorobutadiene; Triphenyl phosphine; Bisulphite glyoxal; Butyl vinyl ether; Tetramethylene sulfone, 99%; Dibutyltindilaurate; Dichloromethyltrimethylsilane; Diethylmethyl phosphonate; Glyoxal sodium bisulfite addition compound monohydrate;

Boron trifluoride etherate; Cyclohexanedione; Toluene-4-sulfonic acid monohydrate; and Methyllithium, 1.4M solution in diethyl ether were used as purchased.

Thin-layer chromatography was carried out using silica-gel UV<sub>254</sub> (0.25mm) plates and the compounds visualised using UV light. Column and flash column chromatography was carried out using silica-gel, 60 A, obtained from Aldrich Chemical Company Ltd.

### **7.1.2 Materials used for electrochemical study**

Supporting electrolytes: Tetrabutylammonium hexafluorophosphate; Tetrabutylammonium bromide; Tetraethylammonium tetrafluoroborate; Tetrabutylammonium tetrafluoroborate; Tetrabutylammonium hydrogen sulfate; Tetraethyl-ammonium p-toluenesulfonate; Lithium perchlorate; Tetrabutylammonium Iodide; and Tetrabutylammonium trifluoromethane sulfonate were supplied from Aldrich Chemical Company Ltd. and dried under reduced pressure at 110 °C for 48 hours before being used in the electrochemical polymerization. Two electrolytes used in the cyclic voltammetric studies, Tetraethylammonium tetrafluoroborate and Tetrabutylammonium hexafluorophosphate, were purified by recrystallization from methanol and 40 - 60°C light petroleum ether<sup>1</sup> and dried under vacuum.

Potassium ferrocyanide; Potassium ferricyanide were used as purchased from Aldrich Chemical Company Ltd.

## **7.2 Solvent Purification**

### **7.2.1 Solvents used for synthesis**

All solvent purifications followed the standard procedures<sup>1,2</sup>. The methods applied are summarised below:

#### **Diethyl ether**

This was first dried by standing over potassium hydroxide pellets overnight, followed by refluxing over sodium and benzophenone for 2 hours, then distilled and used immediately.

#### **Hexane**

Stored over Lindas 3A, molecular sieves, and distilled over sodium wire before used.

#### **Tetrahydrofuran**

Distilled over calcium hydride powder, left for 24 hours, and then redistilled and stored over freshly prepared sodium wire.

### **7.2.2 Solvents used for electrochemical study**

#### **Acetonitrile**

First treated with potassium hydroxide, and dried by shaking with Linde 4A molecular sieve and distilled from calcium hydride.

#### **Dichloromethane**

Pre-dried with calcium chloride, and distilled from calcium sulphonate. Stored away from bright light in a brown bottle with Linde 4A molecular sieve.

## **Propylene carbonate**

Purified by percolation through Linde 5A molecular sieve, followed by distillation under vacuum and stored over molecular sieve.

### **7.2.3 Handling of extremely sensitive chemicals**

In order to ensure safe practices and eliminate contamination by moisture, some chemicals, especially silane derivatives, active metals and alkylmetal; were handled under a dry nitrogen atmosphere or in a Faircrest dry nitrogen glove box.

Liquids were measured and transported via stainless steel needles and Hamilton all glass - teflon fixed, gas tight syringes.

## **7.3 Instruments**

### **FT-IR spectrometer**

All FTIR spectra were recorded on a Nicolet - 205 FTIR spectrometer. The solid samples were ground with KBr and pressed into discs. The liquid samples were sandwiched between potassium bromide plates. The spectra of the neat liquids and solid disc samples were taken via transmission.

### **Nuclear Magnetic Resonance spectrometer**

$^1\text{H}$  and  $^{13}\text{C}$  spectra of the monomers and other compounds were obtained using a Jeol - FX 400 FT instrument with a tunable, multinuclear probe and multidimensional nuclear magnetic resonance function. Tetramethylsilane was normally taken as a reference for  $^{13}\text{C}$  and  $^1\text{H}$  chemical shifts.

Deuterated chloroform was chosen as the NMR solvent unless specified. The magic angle spinning NMR spectra of the conducting polymers were carried out by the SERC NMR service at Durham University.



### **Mass spectrometer**

All the Mass spectra were determined on a VG 20-250 VG MASSLAB Automated Mass spectrometer.

### **UV/Vis. spectrometer**

All solution spectra of the monomers, oligomers and polymers were recorded on a Kontron UVIKON 860 or a Lambda 9 spectrophotometer.

### **UV/Vis.-near IR spectrometer**

The spectra of the polymer powder samples were recorded on a UV-3101PC spectrophotometer with a specular reflectance attachment.

### **X - ray powder diffraction**

The diffraction patterns of the polymer powder and film samples were recorded on a Siemens Diffraktomer D5000,  $\text{CuK}\alpha$ ,  $\lambda = 1.5406\text{\AA}$ .

### **Elemental Analyses**

The analysis of the samples were carried out by MEDAC Ltd.

### **Molecular Weight Measurement**

The molecular weight of the soluble poly(4-methoxyisothianaphthene) was determined by Cookson Technology Centre using GPC(polystyrene standard) in chloroform solution.

### **HPLC**

Monitoring the concentration change of the monomers and formation of the intermediates during the polymerisation of isothianaphthene monomers was carried out using a Milton Roy Consta Metric 3000 solvent delivery system

and a Milton Roy UV spectromonitor 3100 with a Waters 740 Data Module integrator. An APEX Silica 5u column was used, made by Jones Chromatography Ltd.( Catalogue Number 4m25300c).

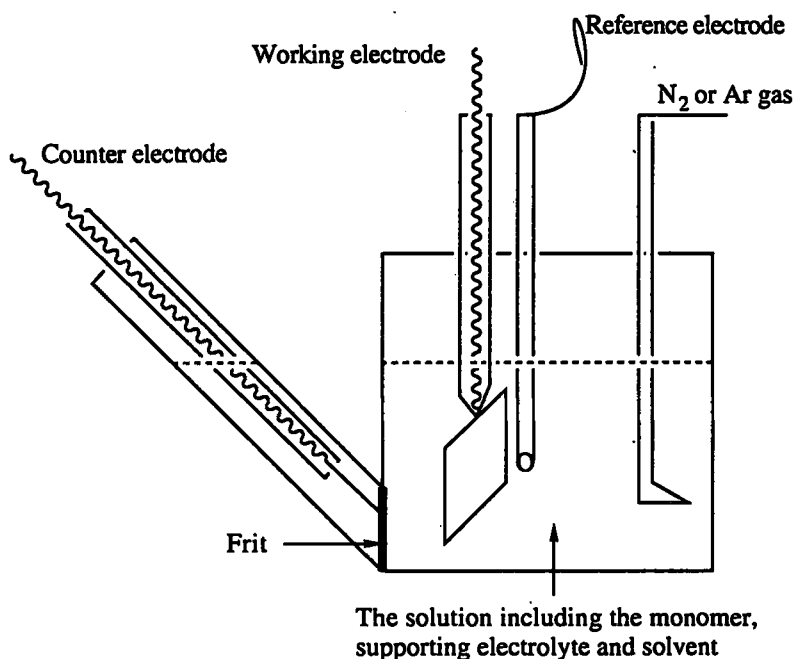
## GC

Capillary(BP5) GC analyses were obtained using a Philips Pye UNICAM PU4500 Chromatograph with a Shimadzu C-R1B chromatopac integrator.

## 7.4 Equipment

### 7.4.1 The electrochemical reaction cell

The electrochemical reaction cell was manufactured in accordance with specifications laid down by Cookson Technology Centre. The outline is shown in Scheme 7-1.



Scheme 7-1 Electrochemical reaction cell

The cell has two compartments separated by a glass frit. The working electrodes were 1 cm or 4 cm square platinum plates; ITO coated conducting glasses were also used. A platinum wire and an Ag/AgCl

electrode were used as an auxiliary and a reference electrode respectively. All measurements of potential, unless otherwise stated, were referenced to the Ag/AgCl electrode.

The procedure for pre-treatment of the electrochemical reaction cell was as follows:

The platinum working and auxiliary electrodes were immersed in a mixture of concentrated HCl and nitric acid (3:1) for about 90 seconds, then washed with tap water, deionised water and acetone successively. The ITO electrode was cleaned in an ultrasonic bath for 15 minutes, immersed in 1% NaOH aqueous solution overnight, followed by washing with deionised water and acetone. The two compartment cell was treated with concentrated HCl and nitric acid (3:1) overnight, washed with tap water continuously for more than 20 minutes, followed by flushing with deionised water and acetone. All of the parts were dried under vacuum.

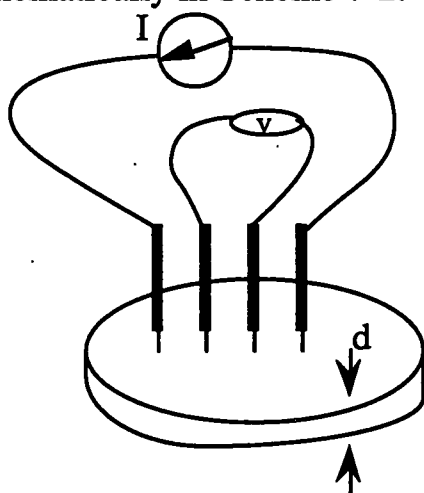
The Ag/AgCl reference electrode was stored in saturated aqueous KCl solution. Before use it was washed with deionised water, followed by washing with acetone. It was dried under a stream of dry nitrogen gas.

#### **7.4.2 Electrochemical apparatus**

The electrochemical experiments, including the cyclic voltammetry, potentiostatic and galvanostatic electrochemical polymerisations, were carried out using an EG & G Princeton Applied Research Model 273A Potentiostat/Galvanostat. This instrument included a programmable voltage - waveform generator and digital coulometer. A wide range of current measurements can be achieved either directly or under computer control.

The cyclic voltammograms were recorded with an Advance Bryans X - Y recorder connected to the potentiostat.

Conductivity measurements of the polymers prepared in this work are performed using a standard 4 probe resistivity bridge as used for semiconductors<sup>3</sup>. The instrument was made in the Open University mechanical workshop according to specifications from Cookson Technology Centre. The 4 probe heads were made from platinum wire. The current source was generated by a mini-potentiostat Model 402 supplied from Sycopel Scientific Ltd. The experimental circuit used for measurement is illustrated schematically in Scheme 7-2.



Scheme 7-2 The four-point probe method for measuring conductivity.

The two outside contacts are used to pass a known current  $I$  while the two inner ones are used to measure the ensuing voltage  $V$ , using a voltmeter with a high input impedance compared to the measured value. The conductivity can be calculated using the equation:

$$\sigma = (I \ln 2)/(V d) \quad (s \gg d)$$

where the thickness  $d$  of the measured sample is much less than the distance  $s$  between the two probes<sup>4</sup>.  $I$  is the applied current and  $V$  is the measured voltage between the two inner probes.

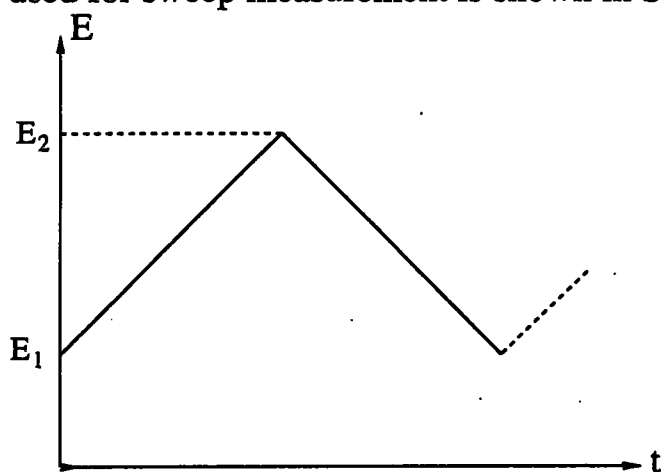
### **7.4.3 Time-resolved UV/Vis absorption spectral and HPLC measurement**

The time-resolved spectral measurements of the polymerisation of isothianaphthene monomers by both electrochemical and pure chemical oxidations were carried out using the same spectrophotometers. The quantitative consumption of the monomers and formation of the intermediates was monitored by normal phase HPLC using a UV detector. The mobile phase was a mixture of spectral grade hexane(80%), dichloromethane(10%) and ethyl acetate(10%). For the electrooxidation, a two compartment cell(50ml) was used and the counter electrode(Pt foil) was separated with a glass frit. The working electrode was a 1x1cm<sup>2</sup> Platinum plate. All solutions were initially purged with nitrogen, then the gas stream was directed over the solution, unless stated otherwise. The reaction cell containing the working electrode was stirred using a magnetic stirring bar during the electrooxidation. A sample(2ml) was collected from the working cell at given intervals for UV/Vis examination using a gas tight syringe under nitrogen protection. After UV/Vis measurement the sample was immediately injected back into the reaction cell. For HPLC testing, 0.1ml of the sample was transferred to a HPLC sample bottle using a gas tight syringe under the protection of nitrogen. The sample was immediately kept at -70°C with dry ice and acetone. It was found that the HPLC of the sample stored at -70°C for 2 hours was the same as that of a sample tested immediately. This enabled us to monitor the change of the monomer and intermediate concentrations. Furthermore, it was noted that the concentrations of all monomers including ITN, DHITN, DMITN, DMDHITN, MeOITN and MeODHITN were linearly proportional to the peak height and peak areas obtained from the HPLC.

In the case of the pure chemical oxidation, the UV/Vis spectra could be obtained in situ in a UV cell under the protection of nitrogen.

## 7.5 Cyclic Voltammetry<sup>5,6,7</sup>

Cyclic voltammetry is a widely used electrochemical analytical technique. The development of a theoretical basis for such measurements has enabled the kinetic parameters of a wide variety of mechanisms to be determined and has allowed the redox potentials of reaction components to be obtained from the 'electrochemical spectrum'. The potential versus time waveform used for sweep measurement is shown in Scheme 7-3.

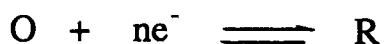


Scheme 7-3 Potential-time profiles for sweep voltammetry.

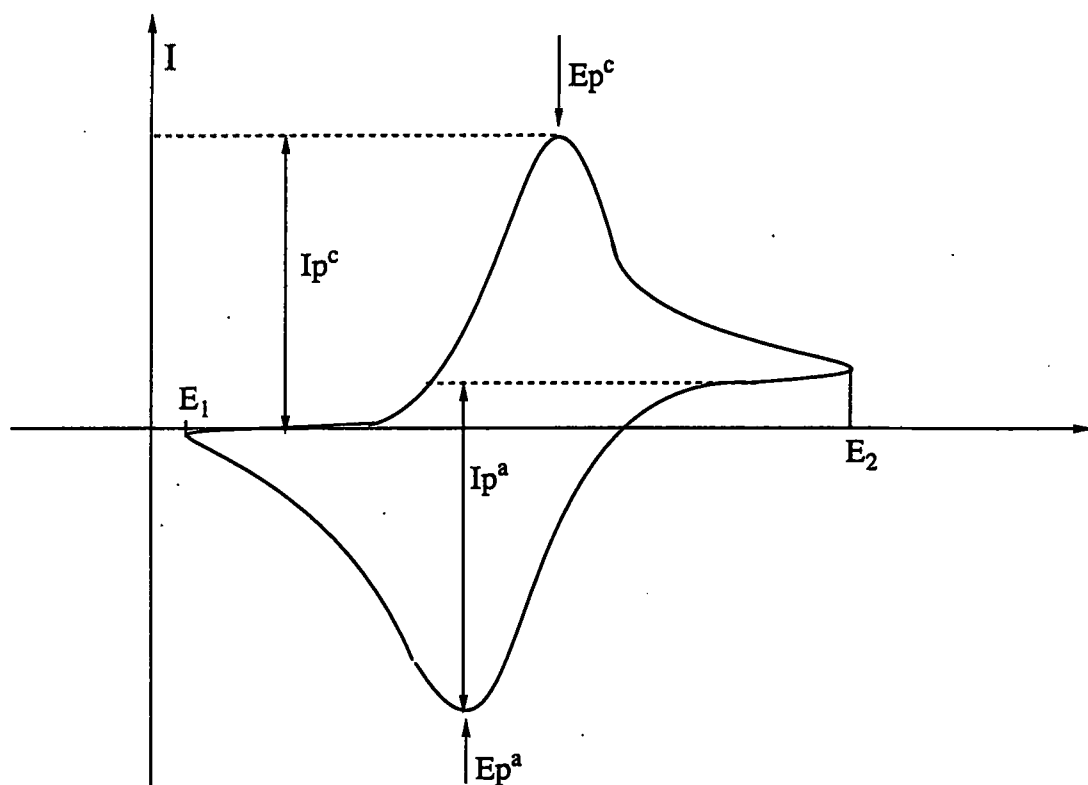
The potential of an electrode is swept from  $E_1$  to  $E_2$  at a known sweep rate  $v$ . When the potential sweep reaches  $E_2$  the sweep is reversed (usually at the same scan rate) until it returns to the initial potential  $E_1$ . The potential sweep can be continued or stopped after completion of one cycle. Whilst the potential is changing the cell current is recorded as a function of the applied potential. The curve of current against potential is referred to as a voltammogram.

### 7.5.1 Reversible reactions

A simple reversible reaction can be described by the equation



When the component O gains one or more electrons it is converted into the component R ( reduction process). If the component R loses an electron it will revert back to the component O. The concentration change of O and R obeys the Nernst equation. A typical voltammogram is shown in Scheme 7-4.



Scheme 7-4 Cyclic voltammogram for a reversible process.

At the beginning of the scan, little or no current is detected (a very small current may be observed due to the change in the electrochemical double layer). As the potential becomes more negative the surface concentration profile of a reactant is increased, and hence the current also rises. The current starts to rise rapidly when the sweep potential approaches the redox potential of the species O. As the species in the vicinity of the electrode becomes depleted, the current falls leading to a peak in the voltammogram. The peak potential  $E_p^c$  is the point where the rate of electron transfer to the

species equals the rate of diffusion of the species towards the electrode. As the potential sweeps past this point the depletion of the species O is faster than the diffusion of the species to the electrode. A depletion layer forms and the current decreases. When the limit  $E_2$  is reached the potential sweep is reversed. At this stage there is a large amount of the species R near the electrode and this species continues to be formed on the reverse sweep until the potential again approaches the point where R begins to be oxidised back to O. The reverse current, thus increases rapidly. With the changing electrode potential the surface concentration of R eventually approaches zero and the current goes through a peak at  $E_p^a$ . It may be found that the total charge related to the oxidation process is lower than that of the forward reduction process. This is because, throughout most of the experiment, there is a concentration difference driving R away from the electrode (only species O is present initially). Most of the product, R, hence diffuses into the bulk solution and cannot be reoxidised on the timescale of the cyclic voltammetric experiment.

The change in the current, on varying the potential, is closely associated with the concentration profile of the electroactive species near the electrode, in order to satisfy the Nernst equation:

$$E = E_0 + \frac{RT}{nF} \ln\left(\frac{[R^e]}{[O^e]}\right)$$

where E is the formal potential of the redox couple and  $[R^e]$  and  $[O^e]$  are the activities of species R and O respectively in the vicinity of the electrode. For a one-electron transfer at 25°C this equation is reduced to :

$$E = E_0 - 0.0059 \log\left(\frac{[R]}{[O]}\right)$$

By solving Fick's 2nd law for O and R the relationship of the peak current density and scan rate at 25°C is as follows:



$$I_p = -2.69 \times 10^{-5} n^{3/2} A D_0^{1/2} C_0 v^{1/2}$$

This is called the Radles-Sevcik equation where  $I_p$ , the peak current density, is in  $A\text{ cm}^{-2}$ ,  $D_0$ , the diffusion coefficient of the species, is in  $\text{cm}^2\text{ s}^{-1}$ ,  $v$ , the potential scan rate is in  $V\text{ s}^{-1}$  and  $A$  is the electrode area. Thus, the peak current is proportional to the concentration of the electroactive species and to the square roots of the sweep rate and diffusion coefficient. Of course, the mathematical treatment is established on the basis that: 1) The rate of the charge transfer process is very fast. 2) There are no coupled chemical reactions involved in the overall electrochemical reaction. 3) Mass transfer of the electroactive species is the only process that determines the flux at the electrode surface<sup>5,6</sup>. The diagnostic criteria for reversible charge transfer is summarised in Table 7-1<sup>5,6</sup>:

Table 7-1 Diagnostic tests for cyclic voltammograms of reversible processes

|  |
|--|
| 1) Properties of the potential:<br>$E_p$ is independent of $v$<br>$E_p^c - E_p^a = 59/n\text{ mV}$ at $25^\circ\text{C}$ and is independent of $v$ |
| 2) Properties of the current function:<br>$i_p/v^{1/2}$ is independent of $v$  |
| 3) Properties of the anodic to cathodic current ratio:<br>$i_p^a/i_p^c$ is unity and independent of $v$  |

### 7.5.2 Irreversible systems

A totally irreversible reaction is one in which the charge transfer process is much slower than the diffusion rate. A quasi-reversible reaction is one where the charge transfer process is controlled by the rate of both diffusion and charge transfer kinetics.

A mathematical treatment of the electrochemical processes of irreversible systems gives rise to the conditions listed in Table 7-2 and Table 7-3:

Table 7-2 Diagnostic tests for totally irreversible system

|   |
|---|
| 1) Properties of the potential:<br>$E_p$ shifts cathodically by $30/\alpha n$ mV for a 10-fold increase in $v$<br>$E_p^c - E_p^a = 59/n$ mV at 25°C and is independent of $v$ |
| 2) Properties of the current function:<br>$i_p/v^{1/2}$ is constant with scan rate, $v$   |
| 3) Properties of the anodic to cathodic current ratio:<br>There is no current on the reverse scan   |

Table 7-3 Diagnostic tests for quasi-reversible system

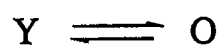
|   |
|---|
| 1) Properties of the potential:<br>$E_p$ shifts with $v$<br>$E_p^c - E_p^a$ may approach $60/n$ mV at a low $v$ but increase as $v$ increases |
| 2) Properties of the current function:<br>$i_p/v^{1/2}$ is virtually independent of $v$   |
| 3) Properties of the anodic to cathodic current ratio:<br>$i_p^a / i_p^c$ equal to unity only for $\alpha = 0.5$                              |
| 4) Other:<br>The response visually approaches that of the irreversible charge transfer as $n$ is increased                                    |

### 7.5.3 Coupled homogeneous reactions

Cyclic voltammetry is also the most powerful technique for investigating coupled chemical reactions and has the advantage that you are able to detect and identify reaction intermediates from the recorded voltammograms. However, coupled homogeneous reactions are more complicated than simple reversible charge transfer reactions and involve both charge transfer (E) and chemical reaction (C), each producing some intermediates. The main types of coupled homogeneous reactions can be divided into four categories;

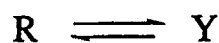
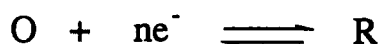
CE , EC, catalytic and ECE. Their reaction equations and cyclic voltammetric properties are outlined below:

### 1) The CE reaction



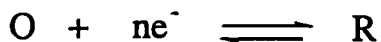
In the voltammogram  $I_p^c/v^{1/2}$  decreases as  $v$  increases, and  $|I_p^a/I_p^c|$  increases with  $v$  and is always greater than, or equal to unity.

### 2) The EC reaction



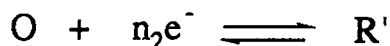
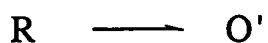
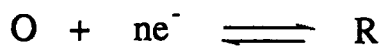
The voltammogram shows that  $|I_p^a/I_p^c|$  is less than one but tends to unity as  $v$  is increased;  $I_p^c/v^{1/2}$  decreases slightly with the increase of  $v$ ;  $E_p^c$  is more positive for the reversible case and will shift negatively with increasing  $v$ , in the pure kinetic region shifting by  $30/n$  mV per 10 fold increase in  $v$  ( this changes to  $19/n$  mV for a second order reaction).

### 3) The catalytic reaction



The properties of such electrochemical processes are that  $|I_p^c|/v^{1/2}$  decreases as  $v$  increases;  $|I_p^a/I_p^c| \ll 1$ ;  $I_p^c$  may reach a limiting value at low sweep rates and  $|I_p^c|$  values are greater than these predicted by the Randles-Sevcik equation.

#### 4) The ECE reaction



The diagnostic tests for ECE reactions are :

$I_p^c/v^{1/2}$  varies with sweep rate but may reach limiting values at high and low sweep rate  $\{|I_p^c/v^{1/2}|(\text{low } v) > |I_p^c/v^{1/2}|(\text{high } v)\}$ ;  $|I_p^a/I_p^c|$  increases with sweep rate and tends to one at a high sweep rate.

### 7.6 Synthesis of Heterocyclic Compounds Containing Sulphur or Silicon

#### 7.6.1 Isothianaphthene and its derivatives

##### 1,3-Dihydrobenzo-[c]-thiophene (DHITN) (1)<sup>8,9</sup>

0.1mol. of finely powdered  $\alpha,\alpha'$ -dibromo-o-xylene was slowly added over 60 minutes in very small portions to a mixture of sodium sulfide nonahydrate (0.1 mol) in 100ml of ethanol (99%) with mechanical stirring under the protection of nitrogen. The hot reaction mixture was allowed to cool down to room temperature. 50ml of water was added and the solution was filtered to remove an amorphous grey precipitate. The filtrate was extracted three times with 200ml of 40 - 60°C petroleum ether. The combined extracts were evaporated to obtain the crude product (55 - 60% yield). The crude product was further purified by vacuum distillation. The final pure product is a white crystalline solid with a melting point below 25°C.

FTIR (neat):  $\nu_{\text{max}} = 3061, 3023, 2912, 2840, 1487, 1454, 1438, 1167, 884, 742, 731$  and  $473 \text{ cm}^{-1}$

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 4.22$  (4H, s,  $\text{CH}_2$ ), 7.18 (4H, s,  $\text{C}_6\text{H}_4$ ).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 37.97$  ( $\text{CH}_2$ ), 140.28, 126.61 and 125.92 ( $\text{C}_6\text{H}_4$ ).

Mass (EI):  $m/z$  (%) = 136 (100%,  $\text{M}^+$ )

### 1,3-Dihydrobenzo-[c]-thiophene-2-oxide (2)<sup>10,11</sup>

Sodium periodate (0.12mol) was mixed with 300ml of 50% aqueous methanol in a 500ml two necked round-bottomed flask using a mechanical stirrer. DHITN (0.1mol) was added to this solution, dropwise, slowly over a period of 40 minutes at 40 - 45°C. After DHITN was added the sodium iodate precipitate slowly formed in the solution. The reaction mixture was then left over night at room temperature. The inorganic salt was removed from the mixture by filtration and the filtrate was evaporated to obtain a solid residue. The residue was recrystallized from ethyl acetate and hexane. A pure crystalline solid with a melting point of 87-89°C (lit.<sup>10</sup> mp 85-87°C) was obtained (85% yield).

FTIR (KBr):  $\nu_{\text{max}} = 3065, 3029, 2957, 2915, 2892, 1478, 1452, 1130, 1034, 877, 739$  and  $470\text{ cm}^{-1}$ .

$^1\text{H}$  NMR( $\text{CDCl}_3$ ):  $\delta = 4.19$ (2H, s,  $\text{CH}_2$ ) 4.23(2H, s,  $\text{CH}_2$ ), 7.34(4H, s,  $\text{C}_6\text{H}_4$ ).

$^{13}\text{C}$  NMR( $\text{CDCl}_3$ ):  $\delta = 59.34$ ( $\text{CH}_2$ ), 135.11, 128.39 and 126.55( $\text{C}_6\text{H}_4$ ).

Mass(EI):  $m/z$ (%) = 152 (100%,  $\text{M}^+$ )

### Isothianaphthene (ITN) (3)<sup>10</sup>

1 g of dihydrobenzo-[c]-thiophene-2-oxide and 1.5 g of activated neutral alumina was mixed by grinding with a mortar and pestle. The mixture was placed in a sublimation apparatus and heated under a vacuum of 25 mm mercury at 120 - 125°C for 45 minutes. During heating white crystals

gathered on the cold finger (85% yield). The product obtained from the cold finger was immediately sealed off under dry nitrogen and stored in a freezer. The melting point of the product was 48-54°C (lit.<sup>10</sup> mp 47-56°C).

FTIR(KBr):  $\nu_{\max}$  = 3092, 3051, 1505, 1427, 1372, 1352, 1225, 1163, 856, 775, 495 and 476  $\text{cm}^{-1}$ .

<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 7.18 (2H, s, CH), 6.85 and 7.36 (two sets of peaks) (4H, m, C<sub>6</sub>H<sub>4</sub>).

<sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 117.50 (CH), 123.04, 124.45 and 139.45 (C<sub>6</sub>H<sub>4</sub>).

Mass(EI):  $m/z(\%)$  = 134(100%, M<sup>+</sup>).

#### 1,2-Di(chloromethyl)4,5-dimethylbenzene (4)<sup>12</sup>

Powdered paraformaldehyde (18.0 g) and 37% hydrochloric acid (125ml) were placed in 250ml two necked round-bottomed flask fitted with a condenser and a mechanical stirrer. The mixture was warmed until the solution went transparent. 21.2 g of o-xylene was added in one portion to the solution. The mixture was refluxed for 20 hours and allowed to cool down to room temperature. The supernatant liquid was decanted and the waxy residue was washed twice with water and dissolved in hexane by heating. The solution was decanted from a small amount of water, dried rapidly with MgSO<sub>4</sub> and filtered while hot. The solution was placed in a cold room and a white crystalline product, mp 95-98°C (lit.<sup>12</sup> mp 96-97°C), was finally obtained (35% yield). The yield could be improved by evaporating the hexane and fractionally distilling the residue in vacuo.

FTIR(KBr):  $\nu_{\max}$  = 3010, 2970, 2944, 2920, 2861, 2730, 1508, 1460, 1440, 1269, 1254, 1138, 1074, 1022, 891, 808 and 688  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR( $\text{CDCl}_3$ ):  $\delta$  = 2.25(6H, s,  $\text{CH}_3$ ), 4.70(4H, s,  $\text{CH}_2$ ), 7.15(2H, s,  $\text{C}_6\text{H}_2$ ).

$^{13}\text{C}$  NMR( $\text{CDCl}_3$ ):  $\delta$  = 19.39( $\text{CH}_3$ ), 43.31( $\text{CH}_2$ ), 132.07, 133.5 and 138.04( $\text{C}_6\text{H}_2$ ).

Mass( $\text{EI}^+$ ):  $m/z(\%)$  = 206, 204 and 202(6, 35, 54,  $\text{M}^+$ ), 169 and 167(39, 100,  $\text{M}^+ - \text{Cl}$ ), 132(67,  $\text{M}^+ - 2\text{Cl}$ ).

#### 5,6-Dimethyl-1,3-dihydrobenzo-[c]-thiophene (DMDHITN) (5)

0.1mol of powdered 3,4-bis(chloromethyl)-o-xylene was slowly added over 60 minutes in very small portions to a mixture of sodium sulfide nonahydrate (0.1mol) and 99% ethanol (100ml) using a mechanical stirrer under the protection of nitrogen at 60 - 70°C. The hot reaction mixture was left to cool to room temperature. 50ml of water was added and the solution was filtered to remove an amorphous grey precipitate. The filtrate was extracted three times with 200ml of 40 - 60°C petroleum ether. The combined extracts were evaporated to obtain a white crystalline solid with a melting point at 65-66°C(40 - 50% yield)(lit.<sup>13</sup>mp 67-68°C).

FTIR(KBr):  $\nu_{\text{max}}$  = 3030, 3008, 2965, 2933, 2917, 2905, 2842, 1494, 1449, 1021, 905, 852, 713 and 428 $\text{cm}^{-1}$ .

$^1\text{H}$  NMR( $\text{CDCl}_3$ ):  $\delta$  = 2.23(6H, s,  $\text{CH}_3$ ), 4.19(4H, s,  $\text{CH}_2$ ), 7.00(2H, s,  $\text{C}_6\text{H}_2$ ).

$^{13}\text{C}$  NMR( $\text{CDCl}_3$ ):  $\delta$  = 19.57( $\text{CH}_3$ ), 37.82( $\text{CH}_2$ ), 125.55, 135.04 and 137.82( $\text{C}_6\text{H}_2$ ).

Mass( $\text{EI}^+$ ):  $m/z(\%)$  = 164(95%,  $\text{M}^+$ ), 149(100,  $\text{M}^+ - \text{CH}_3$ ), 134(20,  $\text{M}^+ - 2\text{CH}_3$ ).

### 5,6-Dimethyl-1,3-dihydrobenzo-[c]-thiophene-2-oxide (6)

A mixture of sodium periodate (0.12mol) and 50% aqueous methanol (300ml) was warmed to 60°C in a 500ml two necked flask fitted with a mechanical stirrer. DMDHITN (0.1mol) was added in very small portions to the solution over a period of 90 minutes. A white precipitate gradually formed with the addition of the DMDHITN. The reaction was kept at this temperature for another 4 hours, then left at room temperature overnight. The reaction mixture was filtered to remove the inorganic salt. The filtrate was evaporated to obtain a solid residue and recrystallised from ethyl acetate and hexane to give white needles with a melting point of 119-120°C (70% yield) (lit.<sup>13</sup>mp 118-119°C).

FTIR(KBr):  $\nu_{\max}$  = 3035, 3009, 2967, 2918, 1496, 1455, 1406, 1384, 1296, 1269, 1210, 1181, 1136, 1126, 1105, 1046, 1026, 913, 895, 846, 699, 681, 620, 573, 531, 506 and 431cm<sup>-1</sup>.

<sup>1</sup>H NMR(CDCl<sub>3</sub>):  $\delta$  = 2.26(6H, s, CH<sub>3</sub>), 4.13(2H, d, J=16Hz, CH<sub>2</sub>), 4.78(2H, d, J=16Hz, CH<sub>2</sub>), 7.12(2H, s, C<sub>6</sub>H<sub>2</sub>).

<sup>13</sup>C NMR(CDCl<sub>3</sub>):  $\delta$  = 19.73(CH<sub>3</sub>), 59.00(CH<sub>2</sub>), 127.41, 132.30 and 137.05(C<sub>6</sub>H<sub>2</sub>).

Mass(EI<sup>+</sup>): m/z(%) = 180(100%, M<sup>+</sup>).

### 5,6-Dimethylbenzo-[c]-thiophene (DMITN) (7)

1 g of the sulfur oxide(6) and 1.5 g of activated neutral aluminum were mixed by grinding with a mortar and pestle. The mixture was placed in a sublimation apparatus and heated in a silica oil bath under a vacuum of 25mm mercury at 130 - 135°C for 45 minutes. During the heating white crystals, mp 76-80°C(lit.<sup>13</sup>mp 77-78°C) were formed on the cold finger



(75% yield). The resulting product was immediately sealed under nitrogen and placed in a freezer.

FTIR(KBr):  $\nu_{\max}$  = 3089, 3019, 2975, 2939, 2912, 2854, 1508, 1440, 1433, 1381, 1199, 860, 740, 407 $\text{cm}^{-1}$ .

$^1\text{H}$  NMR( $\text{C}_6\text{D}_6$ ):  $\delta$  = 2.04(6H, s,  $\text{CH}_3$ ), 7.13(2H, CH), 7.13(2H, s,  $\text{C}_6\text{H}_2$ ).

$^{13}\text{C}$  NMR( $\text{C}_6\text{D}_6$ ):  $\delta$  = 20.34( $\text{CH}_3$ ), 114.78(CH), 120.83, 133.43 and 138.50( $\text{C}_6\text{H}_2$ ).

Mass( $\text{EI}^+$ ):  $m/z(\%)$  = 162(100%,  $\text{M}^+$ ), 147(50,  $\text{M}^+ - \text{CH}_3$ ).

### 2,3-Bis(bromomethyl)anisole(8)<sup>14</sup>

To a solution of 13.6 g of 2,3-dimethylanisole in 200ml of carbon tetrachloride in a 500ml round-bottomed flask was added 35.6 g of N - bromosuccinimide (NBS). The solution was stirred and irradiated with a 100W lamp. After 1 hour irradiation a condenser was placed on the flask and the solution was warmed to reflux until all the NBS was converted into succinimide which floated to the top of the solution. The reaction was stopped and the succinimide filtered off. The filtrate was evaporated to give an oil which solidified on standing. The gummy solid was triturated with two portions of 40 - 60°C petroleum ether to obtain 22 grams of the dibromide product, mp 81-82°C(80% yield)(lit.<sup>14</sup>mp 80-81°C).

$^1\text{H}$  NMR( $\text{CDCl}_3$ ):  $\delta$  = 3.89(3H, s,  $\text{OCH}_3$ ), 4.61(2H, s,  $\text{CH}_2$ ), 4.80(2H, s,  $\text{CH}_2$ ), 6.65 ~ 7.24 (3H, m,  $\text{C}_6\text{H}_3$ ).

$^{13}\text{C}$  NMR( $\text{CDCl}_3$ ):  $\delta$  = 23.76 and 22.96( $\text{CH}_2$ ), 55.94( $\text{OCH}_3$ ), 111.48, 122.82, 125.07, 130.06, 137.98 and 157.92( $\text{C}_6\text{H}_3$ ).

Mass(EI<sup>+</sup>): m/z(%) = 296, 294 and 292(4.7, 9.7, 5.0, M<sup>+</sup>), 215 and 213(98.1, 100, M<sup>+</sup>-Br), 134(77.4, M<sup>+</sup>-2Br)

4-Methoxy-1,3-dihydrobenzo-[c]-thiophene (MeODHITN) (9)

A mixture of sodium sulfide nonahydrate (0.1mol) and 99% ethanol (100ml) was placed in a 250ml three necked flask fitted with a mechanical stirrer under the protection of nitrogen at about 45°C. 0.1mol of the powdered 2, 3 - bis(bromomethyl)anisole was slowly added in small portions to the solution over 45 minutes. The hot reaction mixture was allowed to cool down to room temperature. 50ml of water was added and the solution filtered to remove an amorphous grey precipitate. The filtrate was extracted three times with 200ml of 40 - 60°C petroleum ether. The combined extracts were evaporated to obtain a yellow-white liquid (40% yield).

FTIR(KBr):  $\nu_{\max}$  = 2931, 2835, 1601, 1590, 1479, 1470, 1438, 1320, 1275, 1259, 1078, 767 and 704cm<sup>-1</sup>.

<sup>1</sup>H NMR(CDCl<sub>3</sub>):  $\delta$  = 3.74(3H, s, OCH<sub>3</sub>), 4.15(2H, s, CH<sub>2</sub>), 4.21(2H, s, CH<sub>2</sub>), 6.61 ~ 7.15(3H, m, C<sub>6</sub>H<sub>3</sub>).

<sup>13</sup>C NMR(CDCl<sub>3</sub>):  $\delta$  = 35.26 and 38.44(CH<sub>2</sub>), 55.12(OCH<sub>3</sub>), 107.75, 116.62, 128.36, 128.73, 142.33 and 155.96(C<sub>6</sub>H<sub>3</sub>).

Mass(EI<sup>+</sup>): m/z(%) = 166(100, M<sup>+</sup>), 165(72, M<sup>+</sup>-H), 150(31, M<sup>+</sup>-16), 134(69, M<sup>+</sup>-HOCH<sub>3</sub>).

Anal. Calcd for C<sub>9</sub>H<sub>10</sub>OS: C, 65.03; H, 6.06; S, 19.29. Found: C, 64.95; H, 6.01; S, 19.18.

#### 4-Methoxy-1,3 dihydrobenzo-[c]-thiophene-2-oxide (10)

A mixture of sodium periodate (0.06mol) and 50% aqueous methanol (150ml) was warmed up to 60°C in a 250ml two necked flask fitted with a mechanical stirrer. MeODHITN (0.05mol) was slowly added, dropwise, to the solution over a period of 60 minutes. A white precipitate formed gradually on addition of MeODHITN. The reaction solution was kept at this temperature for another 3 hours, then left at room temperature over night. The inorganic salt was removed by filtration and the filtrate was evaporated to obtain a solid residue which could be recrystallined from ethyl acetate and hexane to give slightly yellow-white needles with a melting point of 79-81°C (50% yield).

FTIR(KBr):  $\nu_{\max}$  = 3200 ~ 2800 (m), 1589, 1483, 1279, 1075, 1049, 1027, 788 and 765  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR( $\text{CDCl}_3$ ):  $\delta$  = 3.84(3H, s,  $\text{OCH}_3$ ), 4.10 ~ 4.29(4H, m,  $\text{CH}_2$ ), 6.79 ~ 7.31(3H, m,  $\text{C}_6\text{H}_3$ ).

$^{13}\text{C}$  NMR( $\text{CDCl}_3$ ):  $\delta$  = 56.35 and 59.73( $\text{CH}_2$ ), 55.39( $\text{OCH}_3$ ), 109.64, 118.25, 123.26, 130.03, 136.98 and 157.26( $\text{C}_6\text{H}_3$ ).

Mass( $\text{EI}^+$ ):  $m/z(\%)$  = 182(59%,  $\text{M}^+$ ), 165(9), 150(4), 134(100), 104(71).

Anal. Calcd for  $\text{C}_9\text{H}_{10}\text{O}_2\text{S}$ : C, 59.32; H, 5.53; S, 17.59. Found: C, 59.29; H, 5.49; S, 17.37.

#### 4-Methoxybenzo-[c]-thiophene (MeOITN) (11)

0.2 g of the sulfur oxide(10) and 0.5 g of activated neutral alumina were mixed by grinding with a mortar and pestle. The mixture was placed in a sublimation apparatus and heated in a silica oil bath under a vacuum of 25mm mercury at 115 - 120°C for 30 minutes. During the heating white

crystals were formed on the cold finger which was cooled with ice and salt. It was stored in a freezer. The melting point of the product was 35-46°C.

FTIR(KBr):  $\nu_{\max}$  = 2928, 2805, 1588, 1528, 1470, 1439, 1254, 1076, 762 and 710  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR( $\text{CDCl}_3$ ):  $\delta$  = 3.91(3H, s,  $\text{OCH}_3$ ), 7.80(H, s, CH), 7.54(H, s, CH), 6.22 ~ 7.21(3H, m,  $\text{C}_6\text{H}_3$ ).

$^{13}\text{C}$  NMR( $\text{CDCl}_3$ ):  $\delta$  = 98.52 and 124.30(CH), 55.10( $\text{OCH}_3$ ), 114.26, 114.92, 116.15, 132.50, 139.63 and 152.91( $\text{C}_6\text{H}_3$ ).

Mass( $\text{EI}^+$ ):  $m/z(\%)$  = 164(100%,  $\text{M}^+$ ), 148(3), 132(72).

Anal. Calcd for  $\text{C}_9\text{H}_8\text{OS}$ : C, 65.82; H, 4.91; S, 19.52. Found: C, 65.68; H, 4.94; S, 19.35.

### Thiodiglycolic ester (12)

75 g of thiodiglycolic acid and 100ml of 99% ethanol were added to 200ml of dry toluene in a 500ml roundbottomed flask connected to a Dean - Stark apparatus. 1.0 ml of concentrated  $\text{H}_2\text{SO}_4$  was added to the solution. The solution was refluxed for more than 10 hours until 18 grams of water was collected. The solvent was removed by a rotatory evaporator. The residue was diluted with hexane, washed with 5% aqueous  $\text{NaHCO}_3$  solution and dried with  $\text{MgSO}_4$ . The final product was obtained by evaporation of the solvent (70% yied).

$^1\text{H}$  NMR( $\text{CDCl}_3$ ):  $\delta$  = 1.13(6H, t,  $J=7\text{Hz}$ ,  $\text{CH}_3$ ), 3.56(4H, q,  $J=7\text{Hz}$ ,  $\text{CH}_2$ ), 4.78(4H, s,  $-\text{S}-\text{CH}_2-$ ).

$^{13}\text{C}$  NMR( $\text{CDCl}_3$ ):  $\delta$  = 13.27( $\text{CH}_3$ ), 32.69( $\text{CH}_2$ ), 60.43( $-\text{S}-\text{CH}_2-$ ), 168.78( $>\text{C}=\text{O}$ ).

### Phenanthrenethiophene dicarboxylic acid (13)<sup>15</sup>

4.0 g of sodium wire were cut into very small pieces in mineral oil, washed with hexane and diethyl ether under dry nitrogen, then, slowly added to 80ml of methanol to form sodium methoxide solution.

The mixture of phenanthrenequinone (10.0 g) and thiodiglycolic ester (4.5 g) was dissolved in a small amount of hot toluene (50ml) and the methoxide solution added in one portion to the mixture. The reaction was kept for 5 days at about 50 - 60°C. The final mixture was diluted with 50ml of water and part of the solvent was removed by means of a rotatory evaporator to give a thick liquid. This was then acidified with concentrated hydrochloride. A mixture of the phenanthrenethiophene diglycolic acid and its ester was precipitated and washed with a large amount of water. To hydrolyse the ester into the acid the mixture was dissolved in aqueous sodium hydroxide solution and heated to reflux. The reaction solution was acidified with concentrated hydrochloride to precipitate the product. The precipitate was washed with water and the final pure product, mp 269-270°C(lit.<sup>15</sup>mp 270°C) was obtained by recrystallisation from ethanol.

FTIR(KBr):  $\nu_{\max}$  = 3058, 3015, 2964, 2930, 2870, 2621, 1679, 1648, 1519, 1443, 1265, 1266, 1206, 1166, 1142, 810, 746, 716 and 524cm<sup>-1</sup>.

<sup>1</sup>H NMR(DMSO):  $\delta$  = 3 groups of peaks, 7.48 ~ 7.78, 8.50 ~ 8.60, 8.92 ~ 9.02(8H, m, CH).

Mass(EI<sup>+</sup>): m/z(%) = 322(6%, M<sup>+</sup>), 305(1, M<sup>+</sup>-OH), 278(100, M<sup>+</sup>-CO<sub>2</sub>), 261(7, M<sup>+</sup>-CO<sub>2</sub>, -OH), 234(100, M<sup>+</sup>-2CO<sub>2</sub>).

### Phenanthrenethiophene (PhITN) (14)

2.0 g of phenanthrenethiophene dicarboxylic acid were ground to a fine powder using a mortar and pestle, then placed in a sublimation apparatus. The apparatus was heated using a heating mantle under vacuum of 0.5 mmHg for about 1 hour. The crude product was collected from the cold finger and purified by flash column chromatography using silica gel with diethyl ether. The melting point of the pure product is 164°C(lit.<sup>15</sup>mp 163°C).

FTIR(KBr):  $\nu_{\max}$  = 3050, 3028, 1468, 1444, 1238, 746 and 716  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR( $\text{CDCl}_3$ ): 8.1(2H, s, CH), 7.51 ~ 7.55, 8.21 ~ 8.22, 8.41 ~ 8.44(8H, m, CH).

$^{13}\text{C}$  NMR( $\text{CDCl}_3$ ):  $\delta$  = 117.04, 123.5, 124.3, 127.0, 127.5, 128.3, 129.5, 135.3 (CH).

Mass(EI<sup>+</sup>):  $m/z(\%)$  = 234(100%, M<sup>+</sup>).

Anal. Calcd. for  $\text{C}_{16}\text{H}_{10}\text{S}$ : C, 82.02; H, 4.30; S, 13.68. Found: C, 81.97; H, 4.32; S, 13.60.

### $\alpha$ -Bromo-o-tolunitrile (15)

0.1mol of o-tolunitrile and 0.1mol of N-bromosuccinimide were mixed with 100ml of carbon tetrachloride in a 250ml roundbottomed flask with stirring. The solution was irradiated with a 100W lamp for 1 hour and refluxed until all of the NBS was converted into succinimide which floated to the top of the solution. After filtration the solvent was removed from the filtrate using a rotatory evaporator. An oil was formed which solidified on standing. The gummy solid was triturated with two portion of 40 - 60°C

petroleum ether to obtain a white crystalline solid, mp 73-74°C(80% yield)(lit.<sup>16</sup>mp 72-74°C).

FTIR(KBr):  $\nu_{\max}$  = 3104, 3075, 2986, 2873, 2820, 2223, 1982, 1948, 1837, 1648, 1595, 1572, 1486, 1449, 1230, 1216, 830, 766, 745, 604, 555 and 474cm<sup>-1</sup>.

<sup>1</sup>H NMR(CDCl<sub>3</sub>):  $\delta$  = 4.64(2H, s, CH<sub>2</sub>), 7.38 ~ 7.67(4H, m, C<sub>6</sub>H<sub>4</sub>).

<sup>13</sup>C NMR(CDCl<sub>3</sub>):  $\delta$  = 29.41(CH<sub>2</sub>), 112.37(-CN), 116.67, 128.91, 130.40, 133.10, 133.28, 141.03(C<sub>6</sub>H<sub>4</sub>).

Mass(EI<sup>+</sup>): m/z(%) = 195 and 197(14.5, 14.3, M<sup>+</sup>), 116(100, M<sup>+</sup>-Br)

#### o-Methylenemercaptobenzoic acid (16)

$\alpha$ -Bromo-o-tolunitrile(15) (0.1mol) was added to a solution of the thiourea (0.13mol) and water (50ml) placed in a 250ml two-necked flask fitted with a stirrer and reflux condenser. The mixture was heated under reflux for about 3 hours until the mixture became homogeneous. A solution of 6 gram of sodium hydroxide in 50ml of water was poured into the reaction and the solution refluxed for a further 2 hours. The mixture was allowed to cool to room temperature and acidified with a cold solution of 5ml concentrated sulfuric acid in 50ml of water. A brown-yellow solid formed on the surface of the solution which was filtered off. The solid was washed with a large amount of water and dried in vacuo(40% yield). The melting point of the product is 179-182°C.

FTIR(KBr):  $\nu_{\max}$  = 3062, 2975, 2875, 2814, 2648, 2585, 1685, 1598, 1574, 1492, 1410, 1303, 1278, 1195, 1082, 924, 754, 708, 654, 580, 544 and 494cm<sup>-1</sup>.

$^1\text{H}$  NMR( $\text{d}_6$ -acetone and  $\text{CDCl}_3$ ):  $\delta = 2.36(1\text{H}, \text{t}, J=8\text{Hz}, -\text{SH}), 4.11(2\text{H}, \text{d}, J=9\text{Hz}, \text{CH}_2), 7.39 \sim 8.02(4\text{H}, \text{m}, \text{C}_6\text{H}_4)$ .

$^{13}\text{C}$  NMR( $\text{d}_6$ -acetone and  $\text{CDCl}_3$ ):  $\delta = 27.63(\text{CH}_2), 168.89(-\text{COOH}), 127.19, 128.16, 130.69, 131.78, 132.87, 144.36(\text{C}_6\text{H}_4)$ .

Mass(EI $^+$ ):  $m/z(\%) = 168(32.2\%, \text{M}^+), 150(100, \text{M}^+ - \text{H}_2\text{O}), 135(55.2, \text{M}^+ - \text{SH})$ .

### Thiophthalide (17)

*o*-Methylenemercaptobenzoic acid(16) (0.1mol) was added to 150ml of dry toluene placed in a 250 ml round bottomed flask connected to a Dean-Stark apparatus. 0.3 gram of toluene-4-sulfonic acid monohydrate was added to the solution. The solution was refluxed for more than 8 hours until 1.8 gram of water was collected from the reaction mixture. The solution was washed with 5% aqueous  $\text{KHCO}_3$  solution and dried with  $\text{MgSO}_4$  overnight. The solvent was removed on a rotatory evaporator and a slight yellow-brown solid was obtained. The resulting product was further purified by recrystallisation from hexane and ethyl acetate, mp 60-61 $^\circ\text{C}$ (lit.<sup>17</sup>mp 58-60 $^\circ\text{C}$ ).

FTIR(KBr):  $\nu_{\text{max}} = 3354, 3085, 2978, 2950, 1685, 1596, 1460, 1418, 1238, 910, 770$  and  $700\text{cm}^{-1}$ .

$^1\text{H}$  NMR( $\text{CDCl}_3$ ):  $\delta = 4.46(2\text{H}, \text{s}, \text{CH}_2), 7.43 \sim 7.83(4\text{H}, \text{m}, \text{C}_6\text{H}_4)$ .

$^{13}\text{C}$  NMR( $\text{CDCl}_3$ ):  $\delta = 35.38(\text{CH}_2), 198.53(>\text{C}=\text{O}), 124.50, 127.02, 128.65, 133.83, 136.48, 147.65(\text{C}_6\text{H}_4)$ .

Mass(EI $^+$ ):  $m/z(\%) = 150(100\%, \text{M}^+), 121(84)$  and  $122(39)$ .



Anal. Calcd. for  $C_8H_6OS$ : C, 63.98; H, 4.03; S, 21.35. Found: C, 63.92; H, 4.01; S, 21.08.

### 7.6.2 Silacyclopentadiene derivatives

#### 1,1-Dimethyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene (TPSCP)(18)<sup>18</sup>

17.9 g (0.1mol) of diphenylacetylene and 0.69 g of lithium (0.1mol) were added to 80ml of dried diethyl ether and stirred for 12 hours. To the mixture was added 400ml of THF. 18 g (0.15mol) of dichlorodimethylsilane in 50ml of THF was then added dropwise. The colour of the solution was yellow at the end of the addition. The solution was left to cool to room temperature and 200ml of water was slowly added with stirring. The mixture was extracted three times with ether. The ether solution was evaporated to dryness in vacuo. A slurry was made by treating the residue with petroleum ether (60-80°C) and the solid was collected by filtration. The yellow-green final product was obtained in 70% yield. The melting point of the resulting product was at 180-181°C (lit.<sup>18</sup>mp181°C).

<sup>1</sup>HNMR(CDCl<sub>3</sub>, ppm):  $\delta$  = 0.47{6H, s, (CH<sub>3</sub>)<sub>2</sub>Si}, 6.68 ~ 7.23(20H, m, Phenyl groups).

Mass (CI<sup>+</sup>)(m/z): 415(100%, MH<sup>+</sup>), 400(32, MH<sup>+</sup>-CH<sub>3</sub>).

#### 1,1,3,4-Tetramethyl-1-sila-3-cyclopentene (TMSCP)(19)<sup>19,20</sup>

56ml (0.5mol) of 2,3-Dimethylbutadiene in 100ml of THF was slowly dropped into a mixture of 60ml (0.5mol) of dimethyldichlorosilane and 24 grams (1mol) of sodium metal in 500 ml of THF with mechanical stirring under the protection of nitrogen. The reaction mixture remained for two days at room temperature. The mixture was diluted with 300ml of diethyl ether. The sodium chloride formed was removed by filtration. The filtrate

was evaporated under reduced pressure to remove the solvents. The residue was distilled at 45°C, 30mmHg(lit.<sup>20</sup> 65°C, 41mmHg) to give 35g of the required product (55% yield).

<sup>1</sup>HNMR(CDCl<sub>3</sub>, ppm):  $\delta$  = 0.13(6H, s, CH<sub>3</sub>-Si), 1.31(6H, s, C-CH<sub>3</sub>), 1.68(4H, s, -CH<sub>2</sub>Si).

<sup>13</sup>CNMR(CDCl<sub>3</sub>, ppm):  $\delta$  = -1.82(CH<sub>3</sub>-Si), 19.30(CH<sub>2</sub>-Si), 25.54(CH<sub>3</sub>-C), 130.58(C=C).

Mass(EI<sup>+</sup>)(m/z): 140(51%, M<sup>+</sup>), 125(100, M<sup>+</sup>-CH<sub>3</sub>).

#### 1,1,3,4-Tetramethyl-1-silacyclopentane-3,4-epoxide(20)<sup>19,21</sup>

A solution of m-chloroperbenzoic acid (50%, 34.2 g, 0.2 mol) in 100ml of diethyl ether was slowly dropped into a solution of 1,1,3,4-tetramethyl-1-sila-3-cyclopentene(19) (14 g, 0.1mol) in 150ml of diethyl ether with stirring at -10°C. The mixture was stirred for 5 hours at this temperature. Saturated NaHSO<sub>3</sub> solution (50 ml) was gently added and the mixture stirred for a further 30 minutes. Saturated NaHCO<sub>3</sub> (100 ml) was next added carefully and stirring was continued for another 10 minutes. The organic layer was separated, washed with 5% aqueous NaOH solution and brine, dried with MgSO<sub>4</sub> and evaporated in vacuo. The crude epoxide was distilled at 67-68°C(27mmHg). The yield was 70%.

FTIR(neat):  $\nu_{\max}$  = 2992, 2957, 2928, 2895, 1455, 1375, 1249, 1220, 1166, 1135, 1056, 1019, 903, 867, 842, 832, 736 and 705 cm<sup>-1</sup>.

<sup>1</sup>HNMR(CDCl<sub>3</sub>, ppm):  $\delta$  = 0.08(6H, s, CH<sub>3</sub>-Si), 1.37(6H, s, C-CH<sub>3</sub>), 0.91(2H, d, J=16Hz, -CH-Si-CH-) and 1.22(2H, d, J=16Hz, -CH-Si-CH-).

<sup>13</sup>CNMR(CDCl<sub>3</sub>, ppm):  $\delta$  = -1.60 and -0.47(CH<sub>3</sub>-Si), 20.33(-CH<sub>2</sub>-Si-), 23.23(CH<sub>3</sub>-C), 69.17(C-C).

Mass(EI<sup>+</sup>)(m/z): 156(9%, M<sup>+</sup>).

1,1,3,4-Tetramethyl-1-silacyclopent-4-en-3-ol (21)<sup>22</sup>

n-Butyllithium in hexane (50 ml, 0.125mol) was slowly added to a solution of dry diethylamine (11.5 g, 0.15mol) in 100 ml of dry pentane with stirring under the protection of nitrogen. After the mixture was cooled to 20°C, 7.8 g (50 mmol) of 1,1,3,4-tetramethyl-1-silacyclopentane-3,4-epoxide(20) in 100 ml of dry diethyl ether was added in one portion. The reaction mixture was refluxed for 6 hours. 50 ml of saturated aqueous NaCl solution was then slowly added, and the brown colour of the organic phase disappeared. The organic layer was separated, washed four times with distilled water and dried with MgSO<sub>4</sub>. The crude product was obtained after removing the organic solvents. Further purification was carried out by vacuum distillation at 86°C(22 mmHg)(lit.<sup>22</sup> 90°C, 24mmHg).

FTIR (neat):  $\nu_{\max}$  = 3359, 2962, 2827, 1365, 1248, 1181, 1069, 1002, 929, 844, 825, 802 and 643 cm<sup>-1</sup>.

<sup>1</sup>HNMR(CDCl<sub>3</sub>, ppm):  $\delta$  = 0.12(3H, s, CH<sub>3</sub>-Si), 0.16(3H, s, CH<sub>3</sub>-Si), 1.36(3H, s, CH<sub>3</sub>-C-C), 1.91(3H, s, CH<sub>3</sub>-C=C), 1.03(1H, d, J=15Hz, CHSi) and 1.26(1H, d, J=15Hz, CHSi), 5.55(H, s, CH=C).

<sup>13</sup>CNMR(CDCl<sub>3</sub>, ppm):  $\delta$  = -1.72 and -0.71(CH<sub>3</sub>-Si), 17.81(CH<sub>2</sub>-Si), 29.86(CH<sub>3</sub>-C-OH) and 31.07(CH<sub>3</sub>-C=C-), 82.26(-C-OH), 126.28(CH=C-) and 166.53(CH<sub>3</sub>C=CH-).

1,1,3,4-tetramethyl-1-sila-2-cyclopentene-4-N-phenylcarbamate(22)<sup>23,24</sup>

2.38 g (20mmol) of phenylisocyanate was added to a solution of 1,1,3,4-tetramethyl-1-silacyclopent-4-en-3-ol(21) (0.32grams, 20mmol) in 50ml of pentane in the presence of a drop of dibutyltin dilaurate with stirring under

the protection of nitrogen. The reaction solution was refluxed for 2 hours. A white precipitate was formed (90% yield) and the solvent was removed by filtration. The white solid product obtained was ready to be used without further purification.

FTIR (neat):  $\nu_{\max}$  = 3471, 3410, 3064, 2960, 2927, 1709; 1490, 1414, 1392, 753, 689 and 590 $\text{cm}^{-1}$ .

$^1\text{H}$ NMR( $\text{CDCl}_3$ , ppm):  $\delta$  = 0.15(3H, s,  $\text{CH}_3\text{-Si}$ ), 0.22(3H, s,  $\text{CH}_3\text{-Si}$ ), 1.47(3H, s,  $\text{CH}_3\text{-C}$ ), 1.89(3H, s,  $\text{CH}_3\text{-C=C}$ ), 1.27(1H, d,  $J=15\text{Hz}$ ,  $\text{CHSi}$ ) and 1.73(2H, d,  $J=15\text{Hz}$ ,  $\text{CHSi}$ ), 5.66(H, s,  $\text{CH=C-}$ ), 6.58(H, s,  $\text{-NH-}$ ), 7.00 ~ 7.39( 5H, m, phenyl).

$^{13}\text{C}$ NMR( $\text{CDCl}_3$ , ppm):  $\delta$  = -1.55 and -0.99( $\text{CH}_3\text{-Si}$ ), 17.94( $\text{CH}_2\text{-Si}$ ), 26.32( $\text{CH}_3\text{-C-OCONHPh}$ ) and 28.73( $\text{CH}_3\text{-C=C-}$ ), 91.66( $\text{-C-OCONHPh}$ ), 123.04( $\text{CH=C-}$ ) and 164.17( $\text{CH}_3\text{-C=CH-}$ ), 118.45, 126.24, 128.84 and 138.21(Phenyl), 152.40( $\text{C=O}$ ).

#### 1,1,3,4-Tetramethylsilacyclopentadiene(TMSCPD)(23)<sup>23</sup>

A solution of 1,1,3,4-tetramethyl-1-sila-2-cyclopentene-4-N-phenylcarbamate(22) (2.85 g, 10mmol) in 100ml of carbon tetrachloride was refluxed for 10 hours. The solvent was evaporated under reduced pressure. The residue was dissolved in hexane and washed with diluted aqueous HCl solution and water, and dried with  $\text{MgSO}_4$  for 1 hour. The drying agent was filtered off and the filtrate was evaporated on the rotary evaporator. The residue was distilled at 58 $^\circ\text{C}$ , 30mmHg(lit.<sup>22</sup> 58 $^\circ\text{C}$ , 30mmHg) to obtain the final product (45% yield).

FTIR (neat):  $\nu_{\max}$  = 3022, 2974, 2963, 2940, 2913, 2852, 1619, 1603, 1520, 1499, 1447, 1431, 1366, 1310, 1245, 1122, 1056, 846, 821, 755, 690, 660, 469,460 and 445 $\text{cm}^{-1}$ .

$^1\text{H NMR}(\text{CDCl}_3, \text{ppm}): \delta = 0.13(6\text{H}, \text{s}, \text{CH}_3\text{-Si}), 2.00(6\text{H}, \text{s}, \text{CH}_3\text{-C}), 5.63(2\text{H}, \text{s}, \text{CH}=\text{C-}).$

$^{13}\text{C NMR}(\text{CDCl}_3, \text{ppm}): \delta = -4.95(\text{CH}_3\text{-Si}), 20.73(\text{CH}_3\text{-C}), 126.51(\text{CH}=\text{C}), 157.157(\text{CCH}_3=\text{CH}).$

Mass(EI<sup>+</sup>)(m/z): 138(21%, M<sup>+</sup>), 123(38, M<sup>+</sup>-CH<sub>3</sub>).

### 7.6.3 Synthesis of Tetrachlorobutadienes

#### Dichloropropenal(24)<sup>25</sup>

A mixture of 110ml of CCl<sub>4</sub>, 50 g of n-butoxyethylene and 0.3 g of azodiisobutyronitrile was placed in a 1000ml two necked round-bottomed flask fitted with a condenser. The mixture was heated to close to its boiling point, whereupon a vigorous reaction occurred for 10 minutes. The mixture was then gently refluxed for two hours. The unreacted CCl<sub>4</sub> was removed and the residue was heated to 150°C until all the HCl was eliminated. The mixture was then slowly distilled at atmospheric pressure using a round-bottomed flask with a 20 cm long column containing spirals. The mixture was heated such that the temperature of the vapours at the top of the column remained below 130°C to give a distillate containing both chlorobutane and the dichloropropenal. Further distillation under atmospheric pressure at 126°C(lit.<sup>25</sup> bp 125°C) gave the pure desired product(55% yield).

$^1\text{H NMR}(\text{CDCl}_3): \delta = 6.45(\text{H}, \text{d}, J=8\text{Hz}, -\text{CH}=\text{C}), 9.86(\text{H}, \text{d}, J=8\text{Hz}, -\text{HC}=\text{O}).$

$^{13}\text{C NMR}(\text{CDCl}_3): \delta = 128.95(=\text{CH}), 144.57(=\text{CCl}_2), 188.02(\text{C}=\text{O}).$

NMR data of intermediates:

#### CCl<sub>3</sub>-CH<sub>2</sub>-CHCl-OC<sub>4</sub>H<sub>9</sub>(24a)

$^1\text{H NMR}(\text{CDCl}_3)$ :  $\delta = 0.93(3\text{H}, \text{t}, J=8\text{Hz}, -\text{CH}_3)$ ,  $1.38 \sim 1.45(2\text{H}, \text{m}, -\text{CH}_2-)$ ,  $1.59 \sim 1.67(2\text{H}, \text{m}, -\text{CH}_2-)$ ,  $3.52 \sim 3.56(2\text{H}, \text{m}, -\text{OCH}_2-)$ , Two group of peaks at  $3.39 \sim 3.51$  and  $3.92 \sim 3.97$  ( $2\text{H}, \text{m}, \text{CCl}_3\text{-CH}_2-$ ),  $5.92 \sim 5.94(\text{H}, \text{q}, J=2\text{Hz}, -\text{CHCl}-)$ .

$^{13}\text{C NMR}(\text{CDCl}_3)$ :  $\delta = 13.71(\text{CH}_3)$ ,  $19.19$  and  $30.82(\text{CH}_2)$ ,  $70.97(\text{OCH}_2-)$ ,  $62.57$  and  $94.01(-\text{CH}_2\text{-CHCl}-)$ ,  $94.87(-\text{CCl}_3)$ .

$\text{CCl}_2=\text{CH-CHCl-OC}_4\text{H}_9$ (24b)

$^1\text{H NMR}(\text{CDCl}_3)$ :  $\delta = 0.93(3\text{H}, \text{t}, J=8\text{Hz}, -\text{CH}_3)$ ,  $1.37 \sim 1.44(2\text{H}, \text{m}, -\text{CH}_2-)$ ,  $1.58 \sim 1.67(2\text{H}, \text{m}, -\text{CH}_2-)$ ,  $3.49 \sim 3.56(2\text{H}, \text{m}, -\text{OCH}_2-)$ ,  $6.23(\text{H}, \text{d}, J=12\text{Hz}, \text{CCl}_2=\text{CH}-)$ ,  $6.19(\text{H}, \text{d}, J=12\text{Hz}, -\text{CHCl}-)$ .

$^{13}\text{C NMR}(\text{CDCl}_3)$ :  $\delta = 13.66(\text{CH}_3)$ ,  $19.09$  and  $30.82(2\text{CH}_2)$ ,  $70.28(\text{OCH}_2-)$ ,  $93.32(-\text{CHCl}-)$ ,  $125.24(=\text{CCl}_2)$ ,  $128.20(=\text{CH})$ .

1,1,4,4-Tetrachlorobutadiene(TCB)(25)<sup>28</sup>

52.4 grams (0.2mol) of triphenylphosphine was added to 500ml of dichloromethane containing 15.4 grams (0.1mol) of  $\text{CCl}_4$  at  $0^\circ\text{C}$ . The solution was stirred for 2 hours. 12.5 grams (0.1mol) of 3,3-dichloropropenal was then added in one portion to the Wittig solution. The solution was left overnight at  $0^\circ\text{C}$ . The mixture was then poured onto silica gel and  $\text{MgSO}_4$  (2:1). Flash chromatography using silica gel with hexane was used to isolate the pure TCB (45% yield).

FTIR(neat):  $\nu_{\text{max}} = 3059, 2836, 1591, 1550, 1241, 898, 850, 634$  and  $609\text{ cm}^{-1}$  (identical to lit.<sup>26</sup> IR spectrum).

$^1\text{H NMR}(\text{CDCl}_3)$ :  $\delta = 6.60(2\text{H}, \text{s}, \text{CH})$ (the single peak at the same position reported in lit.<sup>27</sup>).

$^{13}\text{CNMR}(\text{CDCl}_3)$ :  $\delta = 123.50(=\text{CH})$ ,  $125.15(=\text{CCl}_2)$ .

Mass(EI<sup>+</sup>)(m/z): 190, 192, 194, 196 and 198(58.6, 69.0, 36.3, 10.1, 1.6, M<sup>+</sup>).

A by-product ( $\text{CCl}_2=\text{CH}-\text{CHCl}_2$ )(25a)

FTIR(neat):  $\nu_{\text{max}} = 3016, 2957, 2928, 1615, 1215, 1210, 923, 746, 715, 633 \text{ cm}^{-1}$ .

$^1\text{HNMR}(\text{CDCl}_3)$ :  $\delta = 6.40(\text{H, d, } J=8\text{Hz, } =\text{CH-})$ ,  $6.31(\text{H, d, } J=8\text{Hz, } -\text{CHCl}_2-)$ .

$^{13}\text{CNMR}(\text{CDCl}_3)$ :  $\delta = 65.65(-\text{CHCl}_2)$ ,  $128.82(=\text{CH-})$ ,  $125.86(=\text{CCl}_2)$ .

1-Morpholino-1-cyclopentene(26)

A solution of 42 g (0.5mol) of cyclopentanone, 52.2g (0.6mol) of morpholine and 1.5g of p-toluenesulfonic acid in 120ml of toluene was heated to boiling in a 500ml round-bottomed flask to which was attached a Dean and Stark apparatus. The reaction was heated for 4 hours until 8ml of water had been collected. The mixture was distilled at reduced pressure to give 54g of 1-morpholino-1-cyclopentene (70% yield).

$^1\text{HNMR}(\text{CDCl}_3)$ :  $\delta = 1.80 \sim 1.88(2\text{H, m, CH}_2)$ ,  $2.27 \sim 2.34(4\text{H, m, CH}_2)$ ,  $2.84(4\text{H, t, } J=8\text{Hz, CH}_2)$ ,  $3.68(4\text{H, t, } J=8\text{Hz, CH}_2)$ ,  $3.64(\text{H, t, } J=4\text{Hz, CH=C})$ .

$^{13}\text{CNMR}(\text{CDCl}_3)$ :  $\delta = 22.37, 30.18$  and  $31.21(3\text{CH}_2)$ ,  $48.93$  and  $66.54(4\text{CH}_2)$ ,  $98.20(\text{CH})$  and  $151.62(=\text{C}<)$ .

2-Dichloromethylenecyclopentanone(27)<sup>29</sup>

10.8 g (0.1mol) of 1-morpholino-1-cyclopentene(26) was added to a large excess of carbon tetrachloride in the presence of 2 equivalent of triethylamine, which would act as a scavenger for hydrogen chloride. The

mixture was kept at 60-70°C for 24 hours in total darkness under a nitrogen atmosphere. The triethylamine hydrochloride was filtered out and the dark solution was stirred with water for 10 hours at room temperature. The organic phase was separated and the solvent evaporated under reduced pressure. The residue was combined with the aqueous phase and was steam-distilled to afford the  $\alpha$ -dichloromethylene ketone, mp 50-51°C (lit.<sup>29</sup> mp 49-50°C) (65% yield).

$^1\text{H NMR}(\text{CDCl}_3)$ :  $\delta = 1.89 \sim 1.97(2\text{H, m, CH}_2)$ ,  $2.47(2\text{H, t, } J=8\text{Hz, CH}_2)$ ,  $2.83(2\text{H, t, } J=8\text{Hz, CH}_2)$

$^{13}\text{C NMR}(\text{CDCl}_3)$ :  $\delta = 18.35, 32.56$  and  $40.85(\text{CH}_2)$ ,  $127.79$  and  $133.95$  ( $\text{C}=\text{CCl}_2$ ) and  $200.70(\text{C}=\text{O})$ .

Mass( $\text{EI}^+$ )( $m/z$ ): 164, 166 and 168(92, 57, 10,  $\text{M}^+$ ), 136, 138 and 140(50, 32, 5,  $\text{M}^+-\text{CO}$ ), 129 and 131(95, 29,  $\text{M}^+-\text{Cl}$ ), 108(100,  $\text{M}^+-\text{Cl}$  and  $-\text{C}=\text{O}$ ).

#### $\alpha,\alpha,\alpha',\alpha'$ -Tetrachloromethylene cyclopentane(28)

3.3 g (20mmol) of 2-dichloromethylenecyclopentanone(27) was stirred with triphenylphosphine (20.9 g, 80mmol) in 50ml of anhydrous acetonitrile under nitrogen at 0°C for 30 minutes. 7.2 g (40mmol) of carbon tetrachloride was added in one portion and the mixture was allowed to return to room temperature. The reaction was stirred for 5 hours until TLC showed no triphenylphosphine was left. The solution was diluted with ether, washed twice with water, then with brine, dried and evaporated to dryness. The yield was very low (5%), the rest being the unreacted starting ketone (27).

$^1\text{H NMR}(\text{CDCl}_3)$ :  $\delta = 1.77(2\text{H, p, } J=8\text{Hz, CH}_2)$ ,  $2.56(4\text{H, t, } J=8\text{Hz, CH}_2)$ .



$^{13}\text{C}$ NMR( $\text{CDCl}_3$ ):  $\delta$  =20.93( $-\text{CH}_2-$ ), 33.95( $\text{CH}_2$ ), 115.79 and 136.80( $\text{C}=\text{CCl}_2$ ).

Mass( $\text{EI}^+$ )( $m/z$ ): 230, 232, 234, 236 and 238(10.4, 13.3, 6.3, 1.3, 0.2,  $\text{M}^+$ ), 195, 197, 199 and 201(19.8, 19.0, 6.3, 1.2,  $\text{M}^+-\text{Cl}$ ).

## **7.7 Oxidation of Heterocyclic Compounds with Lewis Acids and Other Chemicals**

The general procedure for oxidation of the monomers can be summarized as follows: 5mmol of the monomer was dissolved in 20ml of dry dichloromethane with magnetic stirring under the protection of nitrogen at room temperature. 10mmol of the oxidant was added to the solution. The reaction was left for one to 4 days. The dark blue or deep purple precipitate was collected by filtration. The crude solid product was extracted first with acetone and then with dichloromethane using a soxhlet apparatus each for 24 hours. The final product was pressed into a disc for conductivity measurement.

Further doping of the low conducting polymers with iodine was carried out using saturated iodine solutions in carbon tetrachloride. The mixture was refluxed for 48 hours. The black solid was filtered by suction and extracted with dichloromethane using a soxhlet apparatus for 24 hours. The further oxidation of the low conducting polymers with chloranil was performed using a saturated chloranil solution in toluene. The mixture was refluxed for 48 hours. The black solid was filtered by suction and extracted with toluene and acetonitrile respectively in a soxhlet apparatus each for 24 hours.

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